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Note on the Rate of Evaporation of small Water-Drops, such as Rain-Drops[1]

By **Tadao Namekawa** and **Tatutoshi Takahashi**

(Received May 27, 1937)

Evaporation into still Air

1. Evaporation of water into still air is Stefan's classical problem.[2] Maxwell's treatment[3] of wet-bulb thermometer with a spherical bulb is applicable without modification in our problem. His result is

$$E=4\pi RD/k.(p_1-p_0) \quad \ldots\ldots(1)$$

Here, E : rate of evaporation,
R : radius of the water drops,
p_1 : saturation pressure at the temperature of evaporating surface,
p_0 : vapour pressure of the surrounding air,
D : diffusion constant,
$k=\frac{P}{\sigma\rho}$; P: Barometric pressure, $\sigma=0.623$, ρ; density of air.

In our case, $E=-\frac{d}{dt}\left(\frac{4}{3}\pi R^3\right)$, therefore we have

$$\left.\begin{aligned}&\frac{dR}{dt}=-\frac{D}{Rk}(p_1-p_0)\\ \text{or}\quad &R^2=R_0^2-2D/k.\ (p_1-p_0)t\end{aligned}\right\}\quad\ldots\ldots(2)$$

where R_0 is the radius of drops at $t=0$.

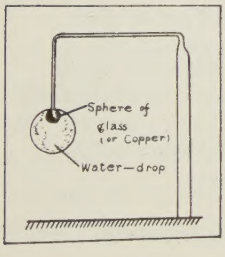
Taking $D=0.24$ while $\rho=0.00129$ gr/cm^3 and $P=760$ mm. Hg.

$$\left.\begin{aligned}&\frac{dR}{dt}=-\frac{2.53\times10^{-7}}{R}(p_1-p_0)\\ \text{or}\quad &R^2=R_0^2-5.06\times10^{-7}(p_1-p_0)t\end{aligned}\right\}\quad\ldots\ldots(2')$$

(R in cm, t in sec., p_1 and p_0 in mm. Hg.)

2. Some simple experimental verification of this result was made by T. Takahashi, one of the authors, in the following way. As shown in Fig. 1, a water drop was attached to the end of a fine stick of glass or copper, and the diminution of its diameter was recorded by a reading micrometer. In order to keep the temperature and humidity of the air uniform, and to prevent its motion, this experiment was conducted in a small box. The humidity was estimated by a hair hygrometer kept

Fig. 1



in comparison with Regnault's dew point apparatus, and also by a dry-and-wet bulb thermometer. For strict accuracy it is of course necessary to know the temperature of the water drop, but as no simple method of estimating it could be devised, the attempt had to be abandoned. Consequently, perfect experimental verification is impossible. Examples of the experimental data obtained are shown in Table 1.

Table 1

No. 1

Date of obs.: 19th Aug. 1931.

Hour	Obs. radius R	Cal. radius R
10 h. 17 m.	0.082 cm.	0.082 cm.
37	0.075	0.075
57	0.068	0.068
11 17	0.060	0.060
37	0.051	0.051

(Glass-suspender)

Dia. of axis = 0.013 cm.
Rad. of sphere = 0.024 cm.
Vapour tension = 19.96 mm. Hg.
Dry-bulb temp. = 26.7°C.
Wet-bulb temp. = 23.9°C.

$$\frac{dR}{dt} = -\frac{4.21 \times 10^{-7}}{R} \qquad \begin{cases} R \text{ in cm.} \\ t \text{ in sec.} \end{cases}$$

$$R^2 = 6.67 \times 10^{-3} - 8.42 \times 10^{-7} t$$

No. 2

Date of obs.: 19th Aug. 1931.

Hour	Obs. radius R	Cal. radius R
13 h. 39 m.	0.080 cm.	0.080 cm.
14 02	0.073	0.073
25	0.065	0.065
48	0.055	0.056
15 11	0.045	0.045

(Glass-suspender)

Dia. of axis = 0.011 cm.
Rad. of sphere = 0.024 cm.
Vapour tension = 20.36 mm. Hg.
Dry-bulb temp. = 26.8°C.
Wet-bulb temp. = 24.2°C.

$$\frac{dR}{dt} = -\frac{4.03 \times 10^{-7}}{R}$$

$$R^2 = 6.43 \times 10^{-3} - 8.05 \times 10^{-7} t$$

No. 3

Date of obs.: 1st Sep. 1931.

Hour	Obs. radius R	Cal. radius R
14 h. 23 m.	0.086 cm.	0.086 cm.
45	0.078	0.078
15 07	0.070	0.069
29	0.059	0.059

(Glass-suspender)

Dia of axis = 0.013 cm.
Rad. of sphere = 0.025 cm.
Vapour tension = 18.29 mm. Hg.
Dry-bulb temp. = 26.1°C.
Wet-bulb temp. = 23.1°C.

$$\frac{dR}{dt} = -\frac{4.89 \times 10^{-7}}{R}$$

$$R^2 = 7.40 \times 10^{-3} - 9.78 \times 10^{-7} t$$

No. 4

Date of obs.: 20th Aug. 1931.

Hour	Obs. radius R	Cal. radius R
13 h. 34 m.	0.066 cm.	0.066 cm.
44	0.061	0.061
54	0.054	0.054
14 04	0.047	0.047
14	0.039	0.039

(Copper-suspender)

Dia. of axis = 0.020 cm.
Rad. of sphere = 0.023 cm.
Vapour tension = 21.50 mm. Hg.
Dry-bulb temp. = 27.0°C.
Wet-bulb temp. = 24.9°C.

$$\frac{dR}{dt} = -\frac{5.91 \times 10^{-7}}{R}$$

$$R^2 = 4.38 \times 10^{-3} - 1.182 \times 10^{-6} t$$

In this table, it is clear that the results accord closely with those arrived at theoretically, namely $R\frac{dR}{dt}=\text{const.}$ In order to ascertain whether this constant agrees with $-D/k.(p_1-p_0)$, the value of p_1 must be estimated. As this has not been done otherwise we calculate the value of p_1 reasoning backward from the formula given above. Then we get what is shown in Table 2. The temperature of the water

Table 2

No.	$R\frac{dR}{dt}$	p_0 mm. Hg.	Dry-bulb Temp. °C	Wet-bulb Temp. °C	p_1-p_0* mm.Hg.	p_1 mm.Hg.	θ_1 °C	λ'
1	-4.21×10^{-7}	19.96	26.7	23.9	1.82	21.78	23.7	0.38
2	-4.03×10^{-7}	20.36	26.8	24.2	1.74	22.10	24.0	0.40
3	-4.89×10^{-7}	18.29	26.1	23.1	2.10	20.39	22.6	0.35
4	-5.91×10^{-7}	21.50	27.0	24.9	2.55	24.05	25.4	2.59

$\left(\frac{k}{D}=4.35\times10^{8}\text{ for this case of }P=752\text{ mm. Hg. and }\rho=0.001165\text{ gr/cm}^3\right)^*$

drop is found to be very close to that of the wet bulb. But in the case of a copper suspender, it is situated between the dry-bulb temperature and the wet-bulb temperature. The heat supplied by conduction, as in the case of the wet-bulb thermometer is $4\pi RK(\theta_1-\theta_0)$. Here $K(\fallingdotseq0.6\times10^{-4})$, which is the thermal conductivity of air. θ_1 is the temperature of the water drops, and θ_0, that of the surrounding air. Assuming the supply of heat other than by conduction to be $\lambda(\theta_0-\theta_1)$, we get the equation of heat balance as follows:

$$p_1-p_0=Kk/LD.\{1+\lambda/4\pi KR\}(\theta_0-\theta_1).....(3)$$

where L is the latent heat of the water. The value of $\lambda'(=\lambda/4\pi KR)$ is, when calculated by the help of this equation, *0.38* in the case of glass, and *2.6* in the case of copper. In view of this it is to be supposed that, in our case, the heat is supplied by conduction from the suspension rather than by radiation.

Evaporation into Moving Air

3. It is important from a meteorological point of view to ascertain the rate of evaporation into moving air as in the case of falling rain drops. A perfect experiment was impossible owing to lack of equipment, but we resorted to a makeshift by turning the set-up described above on the turn table of a gramophone and stopping it only when necessary to read the micrometer. We were able in this way

to carry the experiment up to 2 m/sec. The humidity was measured by means of Assmann's Aspiration Psychrometer and Hair Hygrometer. Two examples of the results of the experiment are shown in Table 3, where the relation $R\frac{dR}{dt}=\text{const.}$ is found to hold. Assuming Assmann's Wet-bulb temperature to be that of the water drop, since this is unknown, we calculated p_1. In order to compare it with the condition in still air, we put

$$R\frac{dR}{dt}=-\beta'\frac{D}{k}(p_1-p_0) \quad \text{.....(4)}$$

and we get the value of β' shown in Table 4, where it is evident that it noticeably increases with the wind velocity.

Table 3

No. 3
Date of obs.: 6th Sep. 1931

Hour	Obs. radius R	Cal. radius R
13h. 45.5m.—14h. 05.5m.	0.085 cm.	0.085 cm.
14 07.5 — 27.5	0.075	0.075
	0.063	0.063
29.5 — 49.5	0.049	0.049

(Glass-suspender No. 2 in the still air exp.)
$v=0.58$ mps. Readings of Assmann's psychrometer
dry 26.32°C
wet 24.35°C
Vapour tension = 21.64 mm. Hg.

$$\frac{dR}{dt}=-\frac{6.80\times10^{-7}}{R} \qquad \begin{cases} R \text{ in cm.} \\ t \text{ in sec.} \end{cases}$$

$$R^2=R_0^2-2A't=0.728\times10^{-2}-1.359\times10^{-6}t$$

No. 8
Date of obs.: 4th Sep. 1931

Hour	Obs. radius R	Cal. radius R
9 h. 28 m.— 9 h. 40 m.	0.083 cm.	0.083 cm.
42 — 54	0.073	0.073
	0.060	0.060
56 —10 08	0.045	0.045

(Glass-suspender No. 2 in the still air exp.)
$v=1.59$ mps. Readings of Assmann's psychrometer
dry 26.00°C
wet 23.52°C
Vapour tension = 20.31 mm. Hg.

$$\frac{dR}{dt}=-\frac{1.139\times10^{-6}}{R}$$

$$R^2=0.690\times10^{-2}-2.278\times10^{-6}t$$

4. It is not easy task to ascertain theoretically the rate of evaporation of a moving water drop. To explain the above experimental fact in the face of various difficulties, we adopted the boundary layer hypothesis, and our discussion is carried on in reference to H. Jeffrey's estimation of the order of the terms of the diffusion equation.[4] He says "If the dimensions of the liquid surface are order of l, and the time needed for any considerable change of condition over it is of order of τ, we see that the terms like $\frac{\partial v'}{\partial t}$, $u\frac{\partial v'}{\partial x}$, and $D\frac{\partial^2 v'}{\partial x^2}$ are relatively orders of $1/\tau$, U/l, and D/l^2." As, inside the boundary layer, U is to be considered extremely small, so

Table 4

No.	v mps.	$R\frac{dR}{dt}$ $\times 10^{-6}$	Assmann		p_1-p_0 mm. Hg.	β'
			Dry °C.	Wet °C.		
1	0.48	−0.571	26.3	24.4	0.97	2.05
2	0.56	−0.766	26.4	24.3	1.04	2.48
3	0.58	−0.679	26.3	24.4	0.98	2.44
4	0.81	−0.792	26.5	24.4	1.03	2.57
5	0.99	−0.850	26.0	23.9	1.03	2.75
6	1.09	−0.889	26.1	24.0	1.07	2.88
7	1.26	−1.063	25.8	23.4	1.22	3.00
8	1.59	−1.139	26.0	23.5	1.21	3.21
9	1.76	−1.098	26.0	24.0	1.01	3.74
10	1.91	−1.244	26.0	23.7	1.15	3.66

$U/l \ll D/l^2$ seems to hold even when $D=0.24$. And on the outside, D is the 10^2-10^3 order and, while, as in our case, $l=10^{-1}$ cm. or thereabout, the relation $U/l \ll D/l^2$ seems to hold even when $U=2\times 10^2$ cm/sec. When $l=10^{-1}$ cm, $1/\tau \ll D/l^2$ is valid on both sides of the boundary layer. From these considerations, the relation of diffusion in this case as the first approximation, may be treated in the following way :

(a) $\frac{d}{dr}\left\{Dr^2\frac{dp}{dr}\right\}=0$ holds on both sides of the boundary layer.

(b) Inside the boundary layer

$p=p_1$ at $r=R$; R is the radius of water drop.

$p=p_b$ at $r=R(1+\delta)$; $R\delta$ is the effective thickness of the boundary layer.

$D=D_0$; D_0 is the coefficient of molecular diffusion.

(c) Outside the boundary layer

$p=p_b$ at $r=R(1+\delta)$

$p=p_0$ at $r\to\infty$

$D=D'$; D' is the eddy diffusion constant, considered as a constant. This assumption is not true, but the influence of this zone on the final result is very small, therefore for simplicity we make the assumption.

The distribution of the vapour pressure satisfying these relations can instantly be obtained, and the rate of evaporation is calculated, after elimination p_b and putting $r=R$:—

$$E=4\pi R\beta D_0/k.(p_1-p_0) \quad (5)$$

Here $$\beta\equiv(1+\delta)/(\delta+D_0/D') \quad (6)$$

If we assume $D_0/D' \ll \delta$, we have

$$\beta=(1+1/\delta) \quad \cdots\cdots(6')$$

This β depends on δ or $R\delta$, which is the effective thickness of the boundary layer, which again depends on the motion of the air. Therefore, according as the velocity increases, δ decreases and the rate of evaporation increases.

From (5) we have

$$R\frac{dR}{dt}=\frac{-D_0\beta}{k}(p_1-p_0) \quad \cdots\cdots(7)$$

which agrees with the experimental equation shown in (4).

5. Next we consider the thermal relations of evaporating water drops. Heat quantity supplied by conduction is

$$Q=4\pi RK(\theta_1-\theta_0)\beta$$

And the heat supplied by other means can be expressed $h=\lambda_m(\theta_1-\theta_0)$. Then we have from the equation of heat balance $EL+Q+h=0$,

$$p_1-p_0=\frac{kK}{LD_0}\left(1+\frac{\lambda_m}{4\pi RK\beta}\right)(\theta_0-\theta_1) \quad \cdots\cdots(8)$$

But as λ_m is unknown, p_1 can not be obtained from this equation. As λ_m seems to be mainly due to the conduction from the suspension stem, we may assume $\lambda_m \fallingdotseq \lambda\beta$ and then $\lambda_m/4\pi RK\beta \fallingdotseq \lambda'$, where we can make use of *0.38*, which is the value of λ' in still air in the case of glass suspension. In this way we obtain p_0 and θ_0 from the equation (8) and then we can calculate p_1 and θ_1. Accordingly we get the value of p_1-p_0 and that of β from the equation (7). The values of β thus obtained are shown in Table 5.

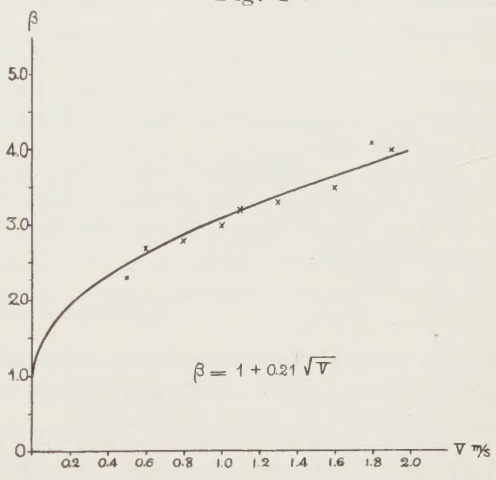
Table 5

No.	v mps.	$R\frac{dR}{dt}$ $\times 10^{-6}$	θ_0 °C.	p_0 mm. Hg.	p_1 mm. Hg.	θ_1 °C.	p_1-p_0 mm. Hg.	β
1	0.48	−0.571	26.3	21.65	22.75	24.5	1.10	2.25
2	0.56	−0.766	26.4	21.51	22.73	24.4	1.22	2.71
3	0.58	−0.679	26.3	21.64	22.74	24.5	1.10	2.66
4	0.81	−0.792	26.5	21.66	22.88	24.5	1.22	2.80
5	0.99	−0.850	26.0	20.99	22.21	24.0	1.22	3.01
6	1.09	−0.889	26.1	21.07	22.29	24.1	1.22	3.15
7	1.26	−1.063	25.8	20.15	21.55	23.5	1.40	3.28
8	1.59	−1.139	26.0	20.31	21.71	23.7	1.40	3.51
9	1.76	−1.098	26.0	21.11	22.27	24.1	1.16	4.09
10	1.91	−1.244	26.0	20.61	21.95	23.8	1.34	4.01

They show no great difference from those reached by way of

Assmann's wet-bulb thermometer. But assumptions remain in both of them. The temperature of the water drop must be measured before the exact value of β is found. The latter depends on the effective thickness of the boundary layer and it would be interesting to investigate their relations. However, it is not allowed to go so deep in discussions from experiments of this kind. More precise experiments are required for such work. The values of β so far ascertained are shown in Fig. 2.

Fig. 2



This can be expressed in the following experimental equation.

$$\beta = 1 + 0.21\sqrt{v} \quad \ldots\ldots\ldots (9)$$
$$(v \text{ in } m/s,\ v < 2.0)$$

Summary

We have made a short theoretical and experimental study concerning the evaporation of a small water drop with a radius under 1 mm.. The decrease of the radius of such a drop due to evaporation can be put in the following equation.

$$\frac{dR}{dt} = \frac{-D\beta}{Rk}.(p_0 - p_0)$$

where

R : radius of water drops,

D : molecular diffusion constant of water vapour into air,

$k = \frac{P}{\sigma\rho}$; P barometric pressure, $\sigma = 0.623$, ρ : density of air,

p_1 : saturation pressure for temperature of water drop,

p_0 : vapour pressure of surrounding air,

β : a constant depending on v, relative velocity of water drop to the air.

Within the limits of experiments, this can be expressed

$$\frac{dR}{dt} = -\frac{2.53 \times 10^{-7}}{R}(1 + 2.11\sqrt{v})(p_1 - p_0).$$

(R in cm., t in sec., v in m/s, $R < 0.1$ cm, $v < 2$ m/s, under ordinary pressure and temperature).

Additional Note

(1) The data of Prof. T. Okada's experiments for the rate of evaporation in still air are found in the "Glazed Frost," a paper published in 1914.[5] His result may be expressed as $R\frac{dR}{dt} = -0.351 \times 10^{-6}$ (C. G. S.) without any deviation.

(ii) The experimental fact that in the evaporation of small liquid drops in moving air the relation $R\frac{dR}{dt}$=const. holds, was noticed in 1931 by Prof. S. Majima[6] and others.

(iii) Mr. Y. Takahasi at the Central Meteorological Observatory of Japan published, in 1935, results of experiments similar to those of the present authors.[7] His discussion showed that $R\frac{dR}{dt}$=const. holds concerning moving air, that the change of shape of water drops in moving air has very little effect on the rate of evaporation, and that the effect of saturation pressure due to surface tension does not appear unless $R=10^{-6}$ cm or less than this. These results are the same as those reached by the present authors, but there are other points on which they have opinions very different from his. It must be added here that, at the first publication of his results, the present authors called his attention to the existence of their unpublished paper and its already published abstract.[8]

(iv) When the authors published the abstract of this paper they adopted $D=0.198$ (from Landolt and Bornsteen's table), but as $D=0.24$ has since been found better, they adopted the latter in the present paper. Hence the difference in coefficient used in the abstract and in the present paper.

(v) Although one of the authors noticed, in a recent number of the Meteorological Magazine, that H. G. Houghten has lately published a paper entitled "A Study of the Evaporation of Small Water Drops," they are not sure what kind of study it is, as they cannot as yet get a copy of the paper.

Literature Cited

(1) The outline of this note was read at the Annual Meeting of the Physico-Mathematical Society of Japan in 1932. Readers may find the abstract of this note in the Appendix of the Proceedings of the Society of that year.

(2) Sitzungsberichte der K. Akad. der Wis. Wien **68** (1873) **73** (1881).

(3) "Diffusion" Encyclopaedia Britannica 9th. ed.

(4) Phil. Mag. **35** (1918) 270.

(5) Jour. of the Met. Soc. of Japan, May 1914 or Monthly Weather Review. (1914) 284.

(6) Riken-iho, **9** 339.

(7) Jour. of the Met. Soc. of Japan July (1935).

(8) loc. cit. (1).

A Method of Obtaining Fibrous Arrangements of the Micro-Crystals of Some Substances

By

Noritomo Matsumoto

(Received June 15, 1937)

Abstract

The writer first dissolved some crystals in water and then soaked a stretched bundle of rayon threads in it. When the crystals were in the act of being recrystallized the solvent was removed by evaporation. How the recrystallization takes place in the interstice of the bundle of rayon threads was the question the writer wanted to examine. He found by means of X-rays that the micro-crystals were reformed in a fibrous form similar to the interstices of the rayon threads. The materials used were potassium chromate, sodium sulphate, potassium bromide, magnesium sulphate and potato starch.

To obtain a fibrous arrangement of the micro-crystals of a substance is very important in examining the lattice form and the nature of the crystal. The writer secured fibrous arrangements of the micro-crystals of some substances which are soluble in water, by recrystallising the solute by evaporating the solvent in the narrow interstices of a stretched bundle of rayon threads. The fibrous arrangement of the micro-crystals thus obtained was examined by means of X-ray diffraction.

The bundle of rayon threads used in the experiment consisted of 400–500 threads, each of which was 7–8μ in diameter. They were fixed on a frame to keep them tense, in the manner shown in Fig. 1, Plate I. After being soaked in an aqueous solution of the substance, the superfluous liquid was removed by stretching the threads as tense as possible, and by means of filter paper. The recrystallization took place slowly by the evaporation of the water solvent in the narrow interstices of the threads. Then the stretched bundle was fixed on the slit of the X-ray camera, and a diffraction photograph was taken by means of a K_α line of copper.

The diffraction pattern due to the rayon threads was of course superposed on the photograph with the impression of the recrystallised substance. But the broadly diffused pattern of the rayon threads was easily discriminated from that of the recrystallised substance.

The materials used were potassium chromate, sodium sulphate, potassium bromide, magnesium sulphate and potato starch. Potato starch was dissolved in water by the Salomon method[1] at ordinary temperature, and the others were all dissolved in water at a temperature of 45–50°C at a concentration of about 2–5%.

Fig. 2, Plate I is the X-ray photograph thus obtained with crystallised potassium chromate, and it is evidently a fibre diagram. The plate distance was 27.6 mm. in this case.

Table I

Layer line	Spots	sin ϕ	I Å	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	Indices	Intensity
0	A_1			.0107	.0097	(110)	st.
	A_2			.0349	.0362	(310)	st.
	A_3			.0671	.0703	(230)	st.
	A_4			.0856	.0869	(330)	m. st.
	A_5			.1019	.1014	(040)	m. st.
1st	I_1	.2641	5.83	.0352	.0355	(021)	st.
	I_2	.2635	5.75	.0688	.0672	(331)	st.
	I_3	.2626	5.87	.1222	.1182	(431)	w.
2nd	II_0	.5122	6.01	.0707	.0705	(302)	st.
	II_1	.5230	5.89	.0951	.0959	(322)	w.
	II_2	.5256	5.86	.1206	.1191	(422)	w.
	II_3	.5306	5.80	.1297	.1300	(512)	st.

Mean value of I=5.88 Å

As shown in Table I, the identity period in the axial direction of the fibre is 5.88 Å, which completely agrees with *a*-axis of the potassium chromate crystal. The lattice form of this crystal belongs to the orthorhombic system, having the size $a=5.88$ Å, $b=10.30$ Å and $c=7.15$ Å, and the micro-crystals nestle in the narrow interstices between the stretched rayon threads by keeping their *a*-axis parallel to the direction of the threads. In the table ϕ is the layer angle and θ is the glancing angle.

Fig. 3, Plate I is the fibre photograph obtained with the crystals of sodium sulphate prepared by the above method. The plate distance was 32.5 mm. in this case.

According to W. H. Zachariasen and G. E. Ziegler[1] the lattice form

1. L. Vanino: Preparative Chemie, Vol. 2, p. 203 (1923).
2. Zeit. f. Krist. Bd. 81. p. 92 (1932).

Plate I

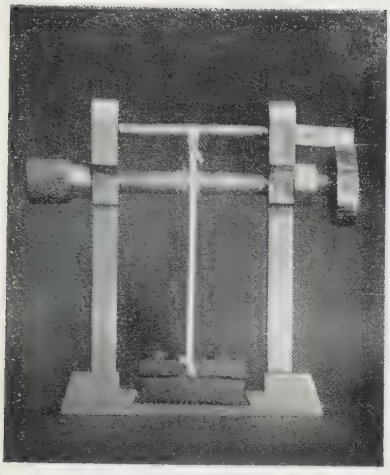


Fig. 1

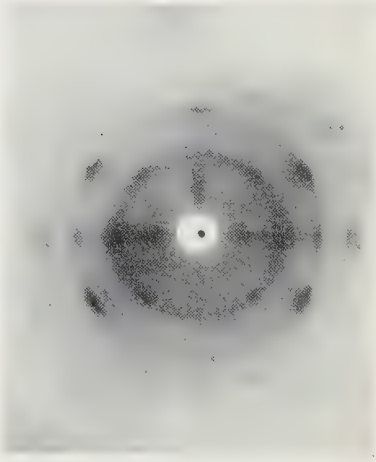


Fig. 2

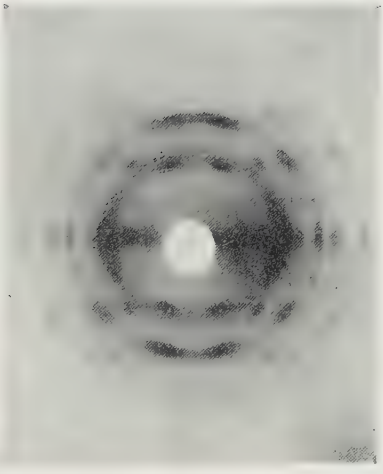


Fig. 3

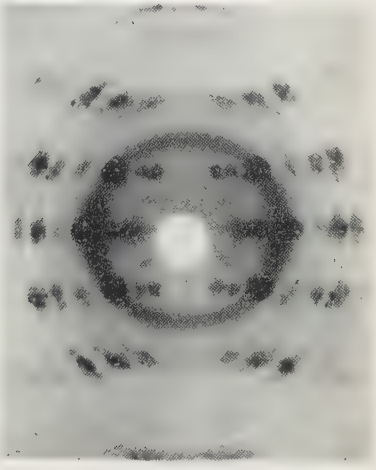


Fig. 4

Table II

Layer line	Spots	sin ϕ	I Å	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	Indices	Intensity
0	A_1			.0406	.0392	(120)	w.
	A_2			.0524	.0524	(020)β	st.
	A_3			.0647	.0628	(020)α	w.
	A_4			.0877	.0862	(140)	st.
1st	I_1	.1378	11.17	.0428	.0415	(031)	w.
	I_2	.1351	11.40	.0532	.0527	(131)	st.
	I_3	.1355	11.37	.0697	.0689	(041)	w.
2nd	II_1	.2671	11.15	.0220	.0235	(102)	st.
	II_2	.2746	11.21	.0411	.0406	(022)	st.
	II_3	.2721	11.32	.0820	.0849	(222)	st.
	II_4	.2688	11.46	.1031	.1045	(232)	w.
3rd	III_1	.4065	11.37	.0477	.0460	(113)	st.
	III_2	.4125	11.20	.0711	.0716	(023)	st.
	III_3	.4085	11.31	.0788	.0793	(213)	w.
	III_4	.4056	11.39	.1118	.1107	(233)	w.
4th	IV_0	.5367	11.47	.0782	.0772	(114)	st.
	IV_1	.5460	11.28	.0891	.0889	(124)	w.
	IV_2	.5411	11.38	.1159	.1151	(024)	st.

Mean value of I=11.3 Å

of the crystal of sodium sulphate is monoclinic, having the size $a=5.85$ Å, $b=12.29$ Å, $c=11.38$ Å and $\beta=59°3'$. The identity period in the axial direction of the fibre, obtained from the photograph, is 11.3 Å and is equal to that in the direction of the c-axis. The positions of the diffraction spots on the photograph agree well with those calculated by taking the c-axis as the fibrous axis of the crystallites in the direction of the stretched threads. The results are tabulated in Table II.

Next, the writer experimented with potassium bromide crystals. Water, alcohol or glycerin may be used as the solvent, for the result is the same in every case. Though the diffraction spots were as not strong as in the former cases, their positions could be measured; and the results are given in Table III.

The identity period in the direction of the fibre is 9.34 Å, which is the same as that of the diagonal of the cube face of the cubic crystal of potassium bromide, whose size is $a=b=c=6.58$ Å. The results are tabulated in Table III. The fibrous arrangement was not perfect in this case, and ordinary Debye-Scherrer rings were superposed on the

Table III

Layer line	Spots	sin ϕ	I Å	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	Indices	Intensity
0	A_1			.0311	.0342	(210)	w.
	A_2			.0425	.0446	(220)β	st.
	A_3			.0551	.0548	(220)α	st.
	A_4			.0882	.0890	(320)	w.
	A_5			.1092	.1096	(400)	st.
1st	I_0	.1661	9.27	.0069	.0069	(001)	w.
	I_1	.1662	9.26	.0403	.0411	(211)	w.
2nd	II_0	.3273	9.40	.0276	.0274	(002)	w.
	II_1	.3307	9.31	.0537	.0548	(202)	st.
	II_2	.3318	9.28	.1167	.1164	(322)	st.
3rd	III_0	.4880	9.46	.0636	.0617	(003)	st.
	III_1	.4972	9.29	.1152	.1165	(223)	st.

Mean value of I=9.34 Å

photograph, which shows the presence of some crystallites oriented entirely at random.

Fig. 4, Plate I is the fibre photograph of the crystallites of magnesium sulphate recrystallised by the above method. The plate distance was 31.6 mm. in this case.

Table IV

Layer line	Spots	sin ϕ	I Å	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	Indices	Intensity
0	A_1			.0164	.0164	(020)	st.
	A_2			.0217	.0208	(210)	st.
	A_3			.0411	.0417	(310)	st.
	A_4			.0632	.0621	(330)β	w.
	A_5			.0762	.0745	(330)α	st.
1st	I_1	.2295	6.71	.0173	.0168	(101)	st.
	I_2	.2274	6.77	.0220	.0209	(111)	st.
	I_3	.2141	7.19	.0289	.0290	(021)	st.
	I_4	.2321	6.64	.0318	.0332	(121)	st.
	I_5	.2256	6.82	.0537	.0537	(131)	w.
2nd	II_1	.4552	6.76	.0662	.0666	(022)	st.
	II_2	.4584	6.72	.0734	.0710	(212)	st.
	II_3	.4636	6.64	.0892	.0871	(032)	st.
3rd	III_1	.6797	6.80	.1349	.1338	(213)	st.
	III_2	.6800	6.79	.1521	.1506	(303)	w.

Mean value of I=6.78 Å

As shown in Table IV, the identity period in the axial direction of the fibre is 6.78 Å, which agrees with that of the c-axis of the orthorhombic crystal of magnesium sulphate having the size $a=11.91$ Å, $b=12.02$ Å and $c=6.87$ Å. Thus the crystallites nestle in the interstices of the stretched rayon threads by keeping their c-axis parallel to the direction of the threads.

Lastly the writer tried to obtain a fibre photograph with soluble potato starch prepared by Salomon's method. The recrystallization of the starch was caused by adding some anhydrous ethyl alcohol to the aqueous potato solution. Though it failed to obtain a clear fibre photograph, an indication of the fibrous arrangement could be detected; and the identity period in the fibrous axis parallel to the direction of the stretched rayon threads was estimated to be about 13 Å. It is hoped that the lattice form of starch may be determined by improving this method in the near future.

In conclusion, the writer wishes to express his sincere thanks to Prof. U. Yoshida for the interest he has taken in the present research.

On the Pseudo-set

By Tameharu Shirai

(Received June 15, 1937)

Let X be a certain set and we shall call its element x, a *point* of set X. Taking X and an object M into consideration, we shall call M a *pseudo-set* with respect to X. For all points x in X and M one of the following three fundamental relations holds:

$$(1)\quad \begin{cases} x \,\bar{\in}\, M, \\ x \,\bar{\notin}\, M, \\ x \parallel M. \end{cases}$$

In the following pages, let us consider that these three fundamental relations and set X are fixed, and we shall call M, shortly, a pseudo-set. When we talk about a point, we mean a point of the set X.

Definition of equality and inequality of pseudo-sets: Two pseudo-sets L and M are called equal, when they satisfy the following conditions. We indicate them by $L=M$:

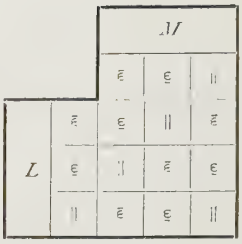
$$(2)\quad \begin{cases} \text{if } x \,\bar{\in}\, L, \text{ then } x \,\bar{\in}\, M, \\ \text{if } x \,\bar{\notin}\, L, \text{ then } x \,\bar{\notin}\, M, \\ \text{if } x \parallel L, \text{ then } x \parallel M, \text{ and vice versa.} \end{cases}$$

By this definition, it is clear that the equality is reflexive, symmetric and transitive. Let for example $L=M$, $M=P$ and $x \,\bar{\in}\, L$, then $x \,\bar{\in}\, M$ for $L=M$, and hence $x \,\bar{\in}\, P$ for $M=P$.

Definition of the sum of two pseudo-sets: If there be an object S satisfying the following properties (3), then it is clear that S is a pseudo-set, and we shall calls S a sum of two pseudo-sets L and M, and denote it by $S=L+M$;

$$(3)\quad \begin{cases} x \,\bar{\notin}\, S \text{ when } x \,\bar{\in}\, L,\ x \,\bar{\in}\, M, \\ x \parallel S \text{ when } x \,\bar{\in}\, L,\ x \,\bar{\notin}\, M, \\ x \,\bar{\in}\, S \text{ when } x \,\bar{\in}\, L,\ x \parallel M, \\ x \parallel S \text{ when } x \,\bar{\notin}\, L,\ x \,\bar{\in}\, M, \\ x \,\bar{\in}\, S \text{ when } x \,\bar{\notin}\, L,\ x \,\bar{\notin}\, M, \\ x \,\bar{\notin}\, S \text{ when } x \,\bar{\notin}\, L,\ x \parallel M, \\ x \,\bar{\in}\, S \text{ when } x \parallel L,\ x \,\bar{\in}\, M, \\ x \,\bar{\notin}\, S \text{ when } x \parallel L,\ x \,\bar{\notin}\, M, \\ x \parallel S \text{ when } x \parallel L,\ x \parallel M. \end{cases}$$

These relations are shown in the accompanying table.



From this definition we obtain the following theorem:

Among three pseudo-sets M_1, M_2 and M_3, we have

$$M_1+M_2=M_2+M_1,$$
$$(M_1+M_2)+M_3=M_1+(M_2+M_3),$$

i. e. the summation of pseudo-sets is commutative and associative.

For let $x \bar{\in} M_1$, $x \underline{\in} M_2$, $x \underline{\in} M_3$ for example, then $x \underline{\in} (M_1+M_2)+M_3$ for $x \parallel (M_1+M_2)$, $x \underline{\in} M_3$, and on the other hand $x \underline{\in} M_1+(M_2+M_3)$ for $x \bar{\in} M_1$, $x \bar{\in} (M_2+M_3)$.

Now let M be a pseudo-set and $\underline{M}$ be an object such as

$$x \underline{\in} \underline{M} \text{ when } x \bar{\in} M,$$
$$x \bar{\in} \underline{M} \text{ when } x \underline{\in} M,$$
$$x \parallel \underline{M} \text{ when } x \parallel M,$$

then, it is clear that $\underline{M}$ is a pseudo-set. We can call $\underline{M}$ a pseudo-anti-set of M. If all points x have the relation "$x \parallel M$" with respect to M, then we can call M a pseudo-zero-set, and we will in general denote it by N. By these definitions, we have

$$M+N=M,$$
$$M+\underline{M}=N.$$

Moreover, it is clear that M is a pseudo-anti-set of $\underline{M}$.

Definition of product of pseudo-sets: if there is an object P which has the following properties (4), then it is a pseudo-set and we shall call P a product of two pseudo-sets L and M, and denote it by $P=LM$:

$$(4)\quad \begin{cases} x \bar{\in} P \text{ when } x \bar{\in} L,\ x \bar{\in} M, \\ x \underline{\in} P \text{ when } x \bar{\in} L,\ x \underline{\in} M, \\ x \parallel P \text{ when } x \bar{\in} L,\ x \parallel M, \\ x \underline{\in} P \text{ when } x \underline{\in} L,\ x \bar{\in} M, \\ x \bar{\in} P \text{ when } x \underline{\in} L,\ x \underline{\in} M, \\ x \parallel P \text{ when } x \underline{\in} L,\ x \parallel M, \\ x \parallel P \text{ when } x \parallel L,\ x \bar{\in} M, \\ x \parallel P \text{ when } x \parallel L,\ x \underline{\in} M, \\ x \parallel P \text{ when } x \parallel L,\ x \parallel M. \end{cases}$$

These relations are shown by the accompanying table.

From this definition, we obtain the following theorem:

Between three pseudo-sets M_1, M_2 and M_3, we have

$$M_1M_2 = M_2M_1,$$
$$(M_1M_2)M_3 = M_1(M_2M_3),$$

i. e. the multiplication of the pseudo-sets is commutative and associative.

For let $x \,\bar{\in}\, M_1$, $x \,\underline{\in}\, M_2$, $x \,\underline{\in}\, M_3$ for example, then $x \,\bar{\in}\, (M_1M_2)M_3$ for $x \,\underline{\in}\, (M_1M_2)$, $x \,\underline{\in}\, M_3$, and on the other hand $x \,\bar{\in}\, M_1(M_2M_3)$ for $x \,\bar{\in}\, M_1$, $x \,\bar{\in}\, (M_2M_3)$.

These two processes, the summation and the multiplication, are also distributive:

$$M_1(M_2+M_3) = M_1M_2 + M_1M_3.$$

For, let $x \,\bar{\in}\, M_1$, $x \,\underline{\in}\, M_2$, $x \,\bar{\in}\, M_3$ for example, then $x \parallel M_1(M_2+M_3)$ for $x \,\bar{\in}\, M_1$, $x \parallel (M_2+M_3)$; on the other hand $x \parallel M_1M_2 + M_1M_3$ for $x \,\underline{\in}\, M_1M_2$, $x \,\bar{\in}\, M_1M_3$.

If all points x have the relation "$x \,\bar{\in}\, M$" with respect to M, we call M a pseudo-unit-set, and denote it by E. From this definition we have

$$\underline{E}\,\underline{E} = E,$$
$$M\underline{E} = \underline{M}.$$

Because, all x have the relation "$x \,\underline{\in}\, \underline{E}$" with respect to $\underline{E}$; therefore $x \,\underline{\in}\, M\underline{E}$, $x \,\bar{\in}\, M\underline{E}$, $x \parallel M\underline{E}$ provided $x \,\bar{\in}\, M$, $x \,\underline{\in}\, M$, $x \parallel M$ respectively.

From the results which we have obtained, we may conclude the following proposition with respect to a system of pseudo-sets $\mathfrak{M}$:

If there exists a pseudo-zero-set in $\mathfrak{M}$, and if the sum and the product of any two pseudo-sets of $\mathfrak{M}$ and the pseudo-anti-set of any pseudo-sets of $\mathfrak{M}$ exist, then the system $\mathfrak{M}$ forms a ring, and if this $\mathfrak{M}$ contains also pseudo-unit-set, then $\mathfrak{M}$ forms a proper ring.

Example of pseudo-set: Let $\mathfrak{F}$ be a system of all one-valued functions $f(x)$ which are defined in the interval $0 < x < 1$, such as

$$f(x_i) = a_i \text{ (integer), for } i = 1,\ 2,\ 3,\ \ldots\ldots,\ n,$$

where $0 < x_1,\ x_2,\ \ldots\ldots,\ x_n < 1$, and let X be the set of these points $x_1,\ x_2,\ \ldots\ldots,\ x_n$. When we define $x_i \,\bar{\in}\, f(x)$, $x_i \,\underline{\in}\, f(x)$ and $x_i \parallel f(x)$, so that $a_i \equiv 1 \pmod 3$, $a_i \equiv 2 \pmod 3$ and $a_i \equiv 0 \pmod 3$ respectively, then it is clear, by the definition of $f(x)$, that these $f(x)$ form pseudo-sets with respect to these three fundamental relations and to the set X. Therefore when we consider $\mathfrak{F}$ as a system of these pseudo-sets, two functions $f_1(x)$ and $f_2(x)$ of $\mathfrak{F}$ such as

$$f_1(x_i) = a_i^{(1)},\ f_2(x_i) = a_i^{(2)} \quad (i = 1,\ 2,\ 3,\ \ldots\ldots,\ n),$$
$$a_i^{(1)} \equiv a_i^{(2)} \pmod 3 \text{ for all } i = 1,\ 2,\ 3,\ \ldots\ldots,\ n,$$

are considered equal: $f_1(x) = f_2(x)$.

Let f_1 and f_2 be any two functions of $\mathfrak{F}$. Then it is clear that $\mathfrak{F}$ contains functions $f_3(x)$, $f_4(x)$ as follows:

$$f_3(x_i) \equiv a_i^{(1)} + a_i^{(2)} \pmod 3, \text{ for all } i = 1, 2, 3, \ldots\ldots n,$$

$$f_4(x_i) \equiv a_i^{(1)} \times a_i^{(2)} \pmod 3, \text{ for all } i = 1, 2, 3, \ldots\ldots n,$$

and these functions $f_3(x)$, $f_4(x)$ are respectively the sum and the product of two pseudo-sets $f_1(x)$ and $f_2(x)$. By this and the definition of $\mathfrak{F}$, it forms a ring and a proper ring, for it contains a pseudo-zero-set, a pseudo-anti-set and the pseudo-unit-set.

At the conclusion we notice that we may give another definition to the sum and the product of pseudo-sets, although they are not fertile.

The author wishes to express his hearty thanks to Professor T. Matsumoto for his valuable advice made during this study.

Change of Lattice Constants of Fibroin by Perfect Drying

By Yoshiaki Matsunaga

(Received June 20, 1937)

Abstract.

Textile fibres were examined by means of X-rays and by measuring their net densities. Fibre and powder photographs were taken when textile fibres were in the ordinary state containing some moisture, and when they were kept perfectly dry in a vacuum camera. It was observed that the lattice of the crystal of silk fibres was somewhat modified by perfect drying, and returned to its original state by regaining the moisture.

The results of measuring the net densities of the fibres in the primary normal alcohols and in water agree very well with those obtained by the X-ray examination.

Introduction

According to Katz[1], textile fibres give exactly the same X-ray photographs whether the fibres are dry or wet. This means that the absorbed water does not penetrate into the interior of the crystal: that is, it causes only intermicellar swelling.

Recently I. Sakurada and K. Hutino[2] examined ramie fibre from which alkali in the mercerised ramie cellulose had been carefully removed by washing; and they observed that the water penetrated into the interior of the crystal lattice, by transforming it into hydrate cellulose. On the other hand K. Sobue[3], who had investigated the hysterisis of an elongation of various kinds of fibres at various humidities, concluded that the swelling phenomena would occur more or less in both intermicellar and intramicellar ways, and that the degree of intramicellar swelling differed in different fibres: natural cellulose fibres showing the smallest, artificial fibres greater, and animal fibres treated by alkali the greatest. An interesting experiment on the hydration and denaturation of the proteins was also carried out by W. T. Astbury and R. Lomax[4]. In their investigation they dried the specimens over phosphorus pentoxide.

1. J. R. Katz: Ergebnis d. exak. Naturwiss., **3**, 374 (1924).
2. I. Sakurada & K. Hutino: Bull. Inst. Phys. Chem. Research (Tokyo) **14**, 171 (1935), and **15**, 973 (1936).
3. K. Sobue: Soc. Chem. Industry Japan, **37**, 1670 (1934).
4. W. T. Astbury & R. Lomax: Jour. Chem. Soc., **54**, 846 (1935).

The apparatus used in the present experiment for drying the specimen was a vacuum camera such as B. Takei[1] employed in examining the starches of rice and potato by means of X-ray. In his experiment Takei observed that the lattices of starch crystals of rice and potato were somewhat modified by perfect drying, and that the lattices thus modified by drying returned to their original state by absorbing moisture. In the present experiment a Cenco Hyvac pump and a mercury diffusion pump were used in evacuating the vacuum camera, in which the specimen was fixed just behind the slit.

Silk fibre is composed of two parts: the sericin in its outer part and the fibroin in its inner part. It had been previously observed by the writer[2] that the lattice of fibroin is changed by perfect drying.

In the present investigation the writer determined the lattice constants of fibroin in the perfectly dry state and in the wet state by means of X-rays; and he measured the net density of the specimens in primary normal alcohols and in water by the evacuation method proposed by U. Yoshida and B. Takei[3], which is especially suited for obtaining the net densities of porous and powdery substances.

X-ray Experiment

1) *Bombyx mori.* First, fibres of silk or *Bombyx mori*, which were stretched to some extent (the same result was obtained with unstretched fibres) and had been soaked in water for two days, were attached behind a pin-hole slit (1.0 m.m. in diameter) of the X-ray camera. To keep them from drying, a cup of water was placed in the camera. In this manner X-ray photographs were taken with the K radiation of Cu or Fe as shown in Fig. 1, Plate I. Table I gives the mean values of the results obtained with many photographic plates and films placed at various distances, 28.5 m.m. or 48.5 m.m. from the specimen.

From the lattice constants of silk fibre obtained by O. Kratky and S. Kuriyama[4] the following quadratic equation is obtained:

$$\frac{4\sin^2\theta}{\lambda^2} = 0.0144h^2 + 0.0204k^2 + 0.0137l^2 - 0.0061hl,$$

where λ is the wave length of the X-rays employed which is ex-

1. B. Takei: Jap. Phys., **8**, 25 (1933).
2. Y. Matsunaga: Die Naturwiss., **24**, 446 (1936).
3. U. Yoshida & B. Takei: These Memoirs, **15**, 1 (1932).
4. O. Kratky & S. Kuriyama: Zeit. phys. Chemie, B, **11**, 363 (1931).

Table I

Spots	Kratky & Kuriyama[1]	Trogus & Hess[2]	ordinary state	100% wet state
	d (A.U.)	d (A.U.)	d (A.U.)	d (A.U.)
A_1	9.17	9.45	8.94	8.80
A_2	4.50	4.81	4.76	4.76
A_3	4.33	4.29	4.21	4.31
A_4	3.07	2.99	2.98	3.04
A_5	2.38	2.35	—	2.31
I_1	5.62	5.53	5.51	5.51
I_2	3.91	3.64	3.81	3.89
I_3	3.62	—	3.63	3.63
I_4	2.25	2.22	—	—
II_0	—	3.45	3.43	3.45
II_1	3.29	3.26	—	—
II_2	2.77	2.74	2.79	2.76
II_3	2.33	2.22	—	—
III_1	2.24	2.27	2.27	2.29
III_2	2.06	2.06	2.06	2.06

pressed by the unit of A. U. and h, k, l are the indices of the atomic planes. The dimension of a unit cell of the fibroin which is used in deducing the above formula is

$a=9.68$ A. U., $b=7.00$ A. U., $c=8.80$ A. U., $\beta=75^\circ 50'$.

The values of $\frac{4\sin^2\theta}{\lambda^2}$ for various spots which were calculated and observed by O. Kratky and S. Kuriyama, were corroborated by the writer in ordinary and 100% wet states; and they are tabulated in Table II. The variation between calculated and observed values in ordinary and 100% wet states does not exceed a reasonable limit of experimental errors. Thus it may be concluded that the lattice constants of silk fibre in an ordinary state containing some water are equal to those in the fully wet state of 100% humidity.

Next, the camera, in which the specimen and the photographic plate or film were set at the same distance as before, was evacuated for many hours by a Cenco Hyvac pump and mercury diffusion pump. After confirming the completed evacuation of the hygroscopic water

1. O. Kratky & S. Kuriyama: loc. cit.
2. C. Trogus & K. Hess: Biochem. Zeit., **230**, 376 (1933).

Table II

Spots	Indices	$\frac{4}{\lambda^2}\sin^2\theta$			Intensity
		Calc.	Observed by Kratky etc.	Observed by the writer in 100% wet	
A_1	100	0.0114	0.0119	0.0124	S
A_2	200	0.0456	0.0481	0.0441	VS
A_3	002	0.0548	0.0533	0.0539	VS
A_4	300	0.1026	0.1062	0.1082	W
A_5	400	0.1824	0.1767	0.1876	VW
I_1	110	0.0318	0.0317	0.0329	W
I_2	210	0.0660	0.0654	0.0660	VW
I_3	012	0.0752	0.0763	0.0759	S
I_4	313	0.1914	0.1976		W
II_0	020	0.0816		0.0840	W
II_1	021	0.0953	0.0924		
II_2	120	0.0930			
II_3	220	0.1227	0.1304	0.1314	W
II_4	022	0.1364			
II_5	320	0.1842	0.1842		
III_0	030	0.1834	0.1842		W
III_1	130	0.1950	0.1992	0.1908	W
III_2	031	0.1973			
III_3	032	0.2384	0.2358	0.2358	W
III_4	230	0.2292			

in the fibres by the Geissler discharge, the X-ray exposure was made by evacuating the camera continuously; and the patterns, differing slightly from those of wet fibroin, as shown in Fig. 2, Plate I, was obtained; as has already been reported by the writer[1]. Generally the diffraction spots diverged a little by perfect drying, and this tendency was especially predominant with the sports III_1 and III_2.

To determine the lattice constants in the perfectly dry state, several X-ray photographs were taken by employing the K radiation of Cu and Fe; and the mean values of the results obtained with many photographic plates and films are given in Table III. The calculated values of $\frac{4\sin^2\theta}{\lambda^2}$ in the table are obtained by the following quadratic equation:

1. Y. Matsunaga: loc. cit.

Table III

Spots	Indices	$\frac{4}{\lambda^2}\sin^2\theta$		Intensity
		Calc.	Observed by the writer	
A_1	100	0.0124	0.0125	S
A_2	200	0.0496	0.0492	VS
A_3	002	0.0576	0.0570	VS
A_4	300	0.1116	0.1126	W
A_5	400	0.1984	0.1941	VW
r_1	110	0.0356	0.0357	W
I_2	011	0.0376		
I_3	210	0.0724	0.0724	VW
I_4	012	0.0808	0.0813	S
I_5	313	0.2096	0.2050	W
II_0	020	0.0928	0.0934	W
II_1	021	0.1072		
II_2	120	0.1052		
II_3	220	0.1422	0.1385	W
II_4	022	0.1504		
II_5	320	0.2034	0.2053	W
III_0	030	0.2088	0.2075	
III_1	130	0.2212		
III_2	031	0.2232	0.2260	W
III_3	230	0.2584	0.2640	W
III_4	032	0.2664		

$$\frac{4\sin^2\theta}{\lambda^2}=0.0124h^2+0.0232k^2+0.0144l^2-0.0062hl,$$

where λ is the wave length of the X-rays which is expressed by the unit of A. U., and h, k, l are the indices of the atomic planes; the above quadratic expression was obtained by taking the dimension of a unit cell of perfectly dry fibroin as

$a=9.19$ A. U., $b=6.63$ A. U., $c=8.56$ A. U., $\beta=76^\circ 43'$,

which is different from that of wet fibroin. As seen in Table III the variation of $\frac{4\sin^2\theta}{\lambda^2}$ between the values calculated and observed is negligible. Consequently it may be concluded that the volume of the unit cell of wet fibroin is greater than that of perfectly dry fibroin, and consequently that the silk fibre manifests intramicellar swelling by absorbing water.

After the diffraction photographs with X-rays were taken by keeping the silk fibres in vacuum camera, air was let into the camera, and diffraction photographs were taken again with the same sample; it was confirmed that the interference spots returned to those of the wet fibroin by absorbing the moisture in the air.

Next some cocoons were boiled in a digester at 155°C for 5 hours. The loss in boiling-off was 40.38% and the net density after boiling was 1.427. With this degree of boiling the sericin may be considered to be almost perfeclty boiled off. The fibroin thus separated from sericin was powdered in a mortar. The powder photographs of perfectly dry and perfectly wet fibroin powder were taken in the manner stated before; they are reproduced in Figs. 3 and 4 in Plate I. The difference between the dry and wet fibroin is clearly perceptible in this case too.

2) Wild Silk. *Altheraca pernyi* and *Antheraca Yamamay* were also examined in the ordinary and the perfecly dry states; and the same difference as in the case of *Bombyx mori* was observed.

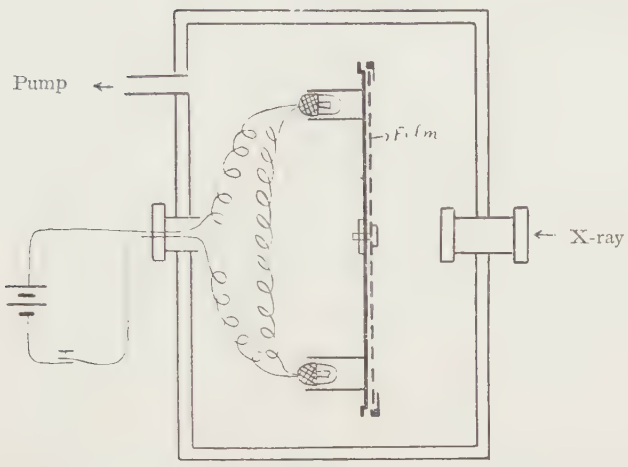
3) Ramie and Artificial Silk. Several experiments on the intramicellar swelling of hydrate cellulose had recently been carried out by I. Sakurada and K. Hutino[1]. The writer also observed the intramicellar swelling of hydrate cellulose. Moreover he observed that ramie also manifested intramicellar swelling. For artificial silk fibre i. e. viscose rayon, Bemberg silk and Nitrocellulose fibre, the swelling was observed to be merely intermicellar.

Measurement of the Contraction of Photographic Film by Evacuation

Now in a vacuum camera the film is dried as well as the sample. Thus the writer attempted to measure the contraction of the photographic film by evacuation. Fig. 1 shows the principle of the apparatus. The film, inserted in the frame of brass, was fixed at its centre with a small brass bolt and a nut. Two small electric lamps were attached, separated sufficiently on the other side of the brass plate at the positions just opposite to the two pin-holes having the diameter of about 0.1 m.m. By these two electric lamps photographic images of the two pin-holes were impressed on the film just below the brass plate. Thus by taking two such photographs, one in the ordinary air and the other in perfectly evacuated and consequently dried state, the

1. I. Sakurada and K. Hutino: loc. cit.

Fig. 1



contraction of the photographic film by evacuation was obtained by measuring and comparing the distances between the images of the two pin-holes on the photographic films. The contraction was found to be about 0.94~0.84% which was very much smaller than the displacement of the diffraction spots by perfect drying observed with fibroin and ramie. Moreover the absence of displacement of the diffraction spots by perfect drying with rayon fibres seems to confirm the view that the displacement of the diffraction spots caused by perfect drying, as was detected with fibroin and ramie, is due really to the change of the size of the unit cell of the crystals.

Consideration from the Net Density

The net densities of silk, ramie and viscose rayon were measured in water and in the primary normal alcohols from methyl alcohol to amyl by the evacuation method devised by U. Yoshida and B. Takei[1]. The results are tabulated in Table IV. As will be seen in the table, points to be noticed are that the net densities of silk fibroin, viscose rayon and ramie decrease with the size of the molecules of various kinds of alcohols, and that the densities of silk fibroin and ramie cellulose which are

Table IV

	Silk (fibroin)	Viscose rayon	Ramie
Water	1.426	1.614	1.614
Methyl alco.	1.483	1.614	1.629
Ethyl alco.	1.445	1.580	1.591
n Propyl alco.	1.382	1.585	1.575
n Butyl alco.	1.380	1.563	1.584
n Amyl alco.	1.382	1.550	1.580

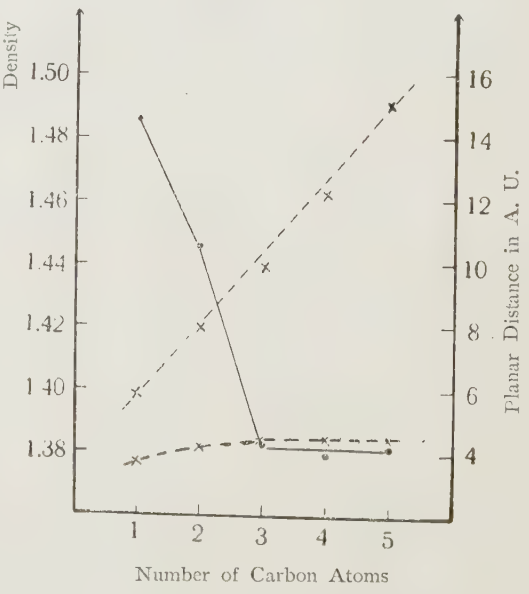
1. U. Yoshida & B. Takei : loc. cit.

measured in water are smaller than those measured in methyl alcohol. This latter fact seems to accord with the view that the intramicellar swelling takes place with silk fibroin and ramie cellulose in water. In the case of viscose rayon, where intramicellar swelling was not detected, the density measured in water is the same as that measured in methyl alcohol.

Next the lattice of perfectly dried silk fibroin soaked with methyl alcohol, was examined by means of the X-ray diffraction. A small glass tube which contained some silk fibroin, was evacuated for hours and then sealed. The silk fibroin thus dried perfectly was soaked with methyl alcohol by breaking the sealed glass tube in methyl alcohol, and then it was sealed in a small thin glass tube. The X-ray examination made on such perfectly dried silk fibroin soaked with methyl alcohol indicated that the crystal lattice was entirely the same as that revealed in the vacuum camera. This fact indicates that the swelling of perfectly dried silk fibroin in methyl alcohol, and probably also in other kinds of primary normal alcohols, is only a intermicellar one.

An investigation on the size of the molecules of primary normal alcohols from methyl to lauryl, has been already carried out by G. W. Stewart and R. M. Morrow[1] Their results are here represented by the broken lines in Fig. 2, by taking the planar distance of ordinates and the number of carbon atoms as absissae. The lower broken line represents the thickness of the molecules, and the upper broken line gives the chain length of the molecules.

Fig. 2



To get a general idea of the relation between the net densities of silk fibroin, which was measured in the alcohols, and the number of the carbon atoms

1. G. W. Stewart & R. M. Morrow: Phys. Rev., **30**, 232 (1927).

of the alcohols, the results of the measurement of the net densities are plotted in Fig. 2, by taking the net densities of perfectly dried silk fibroin as ordinates and the number of carbon atoms of the alcohols in which the density was measured as abscissae. As is evident from the curve thus plotted, the net density of perfectly dried silk fibroin decreases at first as the number of the carbon atoms of the alcohols increases, and then becomes constant when the number of the carbon atoms is more than three, i. e. from propyl alcohol to amyl alcohol.

The reason why the density of perfectly dried silk fibroin decreases with the length of the molecular chain of the alcohols seems to be the increasing difficulty of penetrating into the narrow intermicellar space of the silk with a longer molecular chain.

Discussion

From the experiments above discribed it seems to be certain that the lattice constants of silk fibroin in ordinary air which contains some moisture, or in water, are greater than those in the perfectly dried state. From the following considerations it seems very probable that one molecule of water penetrates into a unit cell of fibroin by intramicellar swelling.

Let ρ_v be the theoretical density of fibroin in a perfectly dry state, then it may be easily calculated by the X-ray data and molecular weight of fibroin.

$$\rho_v = \frac{4 \times 128 \times 1.649 \times 10^{-24}}{507 \times 10^{-24}} = 1.665. \qquad (1)$$

Next, when the penetration of the water molecules by intramicellar swelling into the unit cell is neglected, the theoretical density ρ of fibroin in ordinary wet state, can be calculated from the X-ray data as

$$\rho = \frac{4 \times 128 \times 1.649 \times 10^{-24}}{578 \times 10^{-24}} = 1.461. \qquad (2)$$

If one molecule of water penetrates into a unit cell of perfectly dried fibroin by intramicellar swelling the theoretical density becomes

$$1.461 \times \frac{530}{512} = 1.512. \qquad (3)$$

And the water content is

$$\frac{18}{512} = 3.5\%. \qquad (4)$$

The determination of the water contents of degummed silk, ramie and viscose rayon under ordinary atmospheric conditions in Japan,

namely a relative humidity of 70%—80% was made according to the following methods:

(1) The weight of the specimen in a weighing bottle was measured first, and repeated while drying in a drying oven at 105°C for one hour until constant weight was secured.

(2) A glass bottle containing the specimen was evacuated with a Cenco Hyvac pump at room temperature.

(3) A glass bottle containing the specimen was evacuated with a Cenco Hyvac pump by heating the glass bottle with boiling water.

Results obtained with the alove three methods are tabulated in Table V.

As seen in Table V, the three methods give nearly the same water content at ordinary wet state. As to the volatile matter the writer

Table V

	Ordinary method 105°C 1 hour drying	Vacuum drying at room temperature	Vacuum drying heating with boiling water
Ramie	9.51%	10.35%	10.70%
Silk	10.10	12.56	13.91
Viscose rayon	11.52	13.10	14.98

repeated the drying and moistening several times with the same specimen, and it was found to be negligible as compared with the water contents given in Table V.

As is stated before, the density of the silk fibroin, measured in various kinds of primary normal alcohol, decreases at first with the size of the molecules of the alcohols, and then remains the same with the molecules greater than that of propyl alcohol. This seems to indicate that the intrusion of the alcoholic molecules into the intermicellar space becomes more difficult with increasing molecular size, so that it is almost arrested with alcoholic molecules greater than propyl alcohol. Thus the density of silk fibroin measured in the alcohols whose molecules are greater than propyl alcohol may be used in estimating the porosity due to the existence of the narrow intermicellar space in silk fibroin.

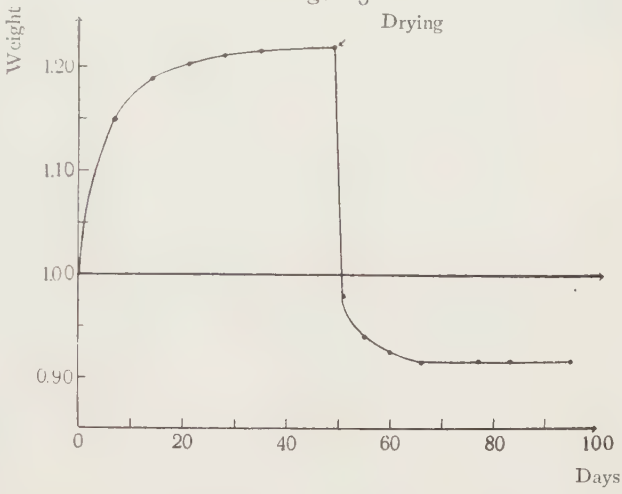
From the theoretical density of perfectly dried fibroin and the apparent density of fibroin measured in normal alcohols, whose molecules are greater than propyl alcohol, the porosity of silk fibroin becomes

$$\frac{1.665-1.380}{1.665}=17.1\%. \qquad (5)$$

Next the writer measured the water content of the silk fibroin

when it was fully wet. About one gram of silk fibroin contained in a weighing bottle was put into a desiccator saturated with water vapour for 49 days, and then it was dried in the desiccator with P_2O_5 for 46 days. By weighing at these two stages the water content of the fibroin at the fully wet state was found to be 30% of the original weight as seen in Fig. 3. This result agrees with that observed by T. Kujirai and his colleagues[1] who observed the water content of silk up to the relative humidity of 95%. As the value of the water content of 30% is that referred to the normal state of the silk fibroin containing the water of about 10%, it becomes 33% when calculated in reference to the perfectly dried state. When silk fibre is fully wet, some water must of course be deposited on the outer surface of the fibre. But if we consider the fact that the silk fibre expands by swelling with water, the absorbing power of silk fibroin for water ought to be considered to be very much stronger in its intermicellar space than on its outer surface. Consequently the amount of water deposited on the outer surface of the fibre is ignored in the following deduction of the amount required for intra- and intermicellar swelling.

Fig. 3



Subtracting the amount of water of 3.5%, which is supposed to have penetrated into the crystal lattice, from the water content of 33% of fully wet fibroin, the quantity of water which intruded into intermicellar space and caused swelling becomes i. e.

$$29.5\%. \qquad (6)$$

Now let us suppose that the silk fibroin is fully wet, then both the intermicellar and the intramicellar swelling are completed. In this

1. T. Kujirai & etc: Bull. Inst. Phys. Chem. Research (Tokyo) **2**, 105 (1924).

case we shall take the net density D of the fibroin micell as $D=1.512$ as stated before. Then the net volume V_1 of the fibroin occupied by its mass M is given by

$$M=V_1D=1.512V_1 \qquad (7)$$

Next let V_2'' be the volume of the intermicellar space occupied by the water swollen perfectly, then from the volume of 29.5% as the weight percentage of the mass of water intruded into the intermicellar space in the fully wet state, we get

$$\frac{V_2''}{1.512V_1}=0.295, \quad \text{or} \quad \frac{V_2''}{V_1}=0.446 \qquad (8)$$

and from (8) we obtain

$$\frac{V_2''}{V_1+V_2''}=\frac{V_2''}{V_1+0.446V_1}=\frac{V_2''}{V_1}\cdot\frac{1}{1.446}=0.309 \qquad (9)$$

This equation means that, when the silk fibroin is fully wet, the volume of the water which has penetrated into the intermicellar space is 31% of the total volume of the fibroin, if we neglect the vacant portion of the narrow intermicellar space into which the water molecules may have intruded.

Silk fibre expands by swelling in water as well as in saturated water vapour. The mean lateral and longitudinal swellings in water of the silk fibroin as used in the present experiment was measured by Prof. Ohara microscopically; and the values of 19.7% and 1.3% were obtained respectively.

Now let V_2 be the volume of the intermicellar space in the air when the expansion of the silk fibre by swelling is negligible, and $\alpha V_2''$ be the vacant portion of the intermicellar space into which the water molecules can not intrude in the fully swollen state, then we have from the above data of swelling,

$$V_1+V_2''+\alpha V_2''=(1.197)^2(1.013)(V_1+V_2),$$
$$=1.451(V_1+V_2), \qquad (10)$$

$$\therefore \quad 1+\frac{V_2''}{V_1}(1+\alpha)=1.451+1.451\frac{V_2}{V_1}. \qquad (10)'$$

By substituting the value of $\frac{V_2''}{V_1}$ into (10)′ we get

$$1.446+0.446\alpha=1.451+1.451\frac{V_2}{V_1} \qquad (11)$$

If we take $\alpha=0.17$ as will be stated later this equation becomes

$$1.522=1.451+1.451\frac{V_2}{V_1},$$

and we get

$$\frac{V_2''}{V_1}=0.049.$$

Next let us consider the reason why the net densities of the fibroin in alcohols are greater than in water. As already explained, the main cause for it is of course the fact that when the silk fibroin dried fully by evacuation is put into the water, one molecule of water per unit cell penetrates into the lattice of the fibroin. In the net density measurement in water before stated this structural change was disregarded. But a second cause lies in the fact that there are some very narrow, vacant cavities in the intermicellar space which can not be occupied by the water molecules even of liquid water.

Let the mass of the silk fibroin dried perfectly in vacuum be M, the mass of water which penetrated into the crystal lattice of fibroin be m, net volume of the silk fibroin which absorbed one water molecule per its unit cell be V_1, the volume of the vacant cavities into which the water molecules can not penetrate be aV_2'' and the net density of the wet silk fibroin be D, then the calculation of the density measurement by evacuation in which we had disregarded the intramicellar swelling was made with the equation

$$\frac{M}{M-\{(M+m)-(V_1+aV_2'')\}}=\frac{M}{M-\left\{(M+m)-\frac{M+m}{D}\left(1+a\frac{V_2''}{V_1}\right)\right\}}=1.426,$$

i. e.

$$\frac{D}{\left(1+\frac{m}{M}\right)\left(1+a\frac{V_2''}{V_1}\right)-\frac{m}{M}D}=1.426$$

By putting $D=1.512$ and $\frac{m}{M}=0.035$ as is stated before in the above equation we get

$$a\frac{V_2''}{V_1}=0.0764;$$

and by giving the value of $\frac{V_2''}{V_1}=0.446$ we have

$$a=0.17=17\%.$$

This shows that the volume of the vacant intermicellar space is 17% of the water which has penetrated completely into the intermicellar space; and consequently that the volume of the vacant intermicellar space is 14.5% of the total volume of the whole intermicellar space when the silk fibroin is swollen completely.

In the above consideration we have assumed that the number of

the water molecules which penetrated intermicellarly into the crystal lattice of fibroin was one per unit cell. If we take the number of water molecules as two or more, then the value of a becomes more than 0.39. This seems to be too large for the volume of the vacant intermicellar space into which the water molecules can not penetrate; and consequently it seems to be more accurate to take the number of the water molecules as one per unit cell of the fibroin crystal, as assumed before.

It may be considered from the above investigation that there are intermicellar spaces of various widths in silk fibroin; and the upper limit of their width is estimated to be of about 10 A. U. from the value of its density measured in alcohols.

When the density of the silk fibroin in alcohols is measured, the swelling has taken place only in the intermicellar manner; and the difference in the values of the densities obtained with different kinds of alcohols seems to be caused by the difference in the degree of intrusion of the alcohols into the intermicellar space as was considered before.

Let V_1 be the net volume of the fibroin, V_2'' the volume of the intermicellar space, aV_2'' the volume of the intermicellar space into which alcoholic molecules can not penetrate, and d be the densities of the silk fibre which we measured in primary normal alcohols; then we get

$$\frac{1.665V_1}{V_1+aV_2''}=d,$$

or

$$\frac{1.665}{d}=1+a\frac{V_2''}{V_1}.$$

The numerical value of $\frac{V_2''}{V_1}$ is obtained from the equation (5)

Table VI

Alcohol	Density	a %
Methyl	1.483	59.2
Ethyl	1.445	44.3
n Propyl	1.382	98.2
n Butyl	1.380	100.1
n Amyl	1.382	98.2

$$\frac{V_2''}{V_1+V_2''}=0.171,$$

$$\therefore\quad \frac{V_2''}{V_1}=0.206$$

and then we get

$$\frac{1.665}{d}=1+0.206a.$$

Table VI shows the values of a thus obtained for various kinds of alcohols.

Summary

The main results obtained from the present experiment are summarised below.

(1) The lattice constant of the silk fibroin in the perfectly dried state is less than that in the wet state; and consequently it may be said that the fibroin brings about the intramicellar swelling by absorbing water.

(2) In the wet state one molecule of water penetrates into the unit cell of perfectly dried fibroin.

(3) This change is reversible.

(4) Even with the evacuation method the density measurement by dipping a fibrous substance into a liquid is not perfect, owing to the presence of very narrow intermicellar spaces into which the liquid molecules can not intrude.

(5) The width of the intermicellar space of different fibrous substances such as ramie cellulose, silk fibroin and viscose rayon is not uniform; and in the case of silk fibroin it varies from zero to about 10 A. U.

In conclusion the writer wishes to express his sincere gratitude to Pr f. U. Yoshida for his kind guidance and invaluable suggestions during the course of his research. His hearty thanks are also due to his friend Mr. T. Matsumoto for his kindness in examining the powder photographs with the microphotometer and he further wishes to say that he is grateful to Prof. K. Ohara for the pains he has taken in measuring the swelling of silk fibre in water with the microscope.

Industrial Physical Laboratory, Nagoya Commercial College.

(April 29, 1937)

Plate I

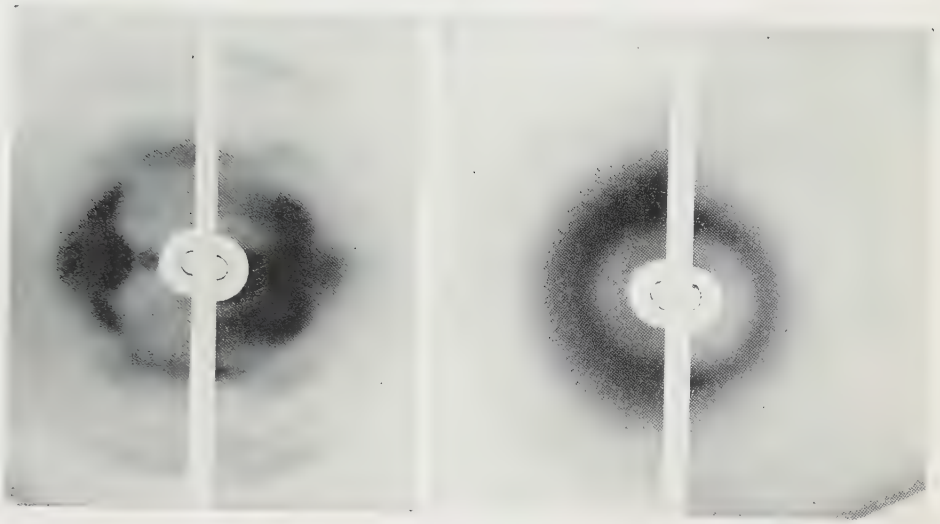


Fig. 1 (wet) Fig. 2 (dry) Fig. 3 (wet) Fig. 4 (dry)

Fig. 5

1 : Microphotometer curve of Fig. 3.
2 : Microphotometer curve of Fig. 4.

Elastic Limit of an Aluminium Rod and the Size of the Crystal Grains

By

Miyabi Sugihara

(Received June 20, 1937)

Abstract

The limit of elasticity of an aluminium rod composed of a single crystal scarcely varies with the difference of the orientation of the crystal. If it varies, the amount of the variation is relatively small. In the case of rods composed of comparatively large crystals, the limit of elasticity decreases rapidly with the increase of the linear crystal size, but after exceeding the crystal size of about 0.3 cm., it decreases very slowly. For the determination of the elastic limit of a rod composed of a large crystal, the method of gradually increasing loads is preferable to that in which the load is applied and removed repeatedly.

Experimental Method

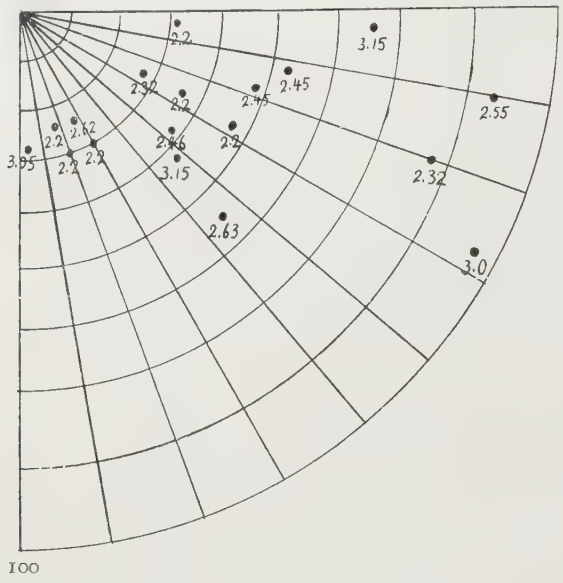
Ten commercial cold-worked aluminium rods about 20 cm. in length and about 5 mm. in diameter were put into the electric furnace together, and heated at about 400°C for two days. When cooled to the room temperature, they were taken out of the furnace. After being elongated by a certain percentage ranging between 0.5% and 24%, they were heated in the furnace again for two days at about 640°C. Thus they were recrystallized. Eight different groups of rods were elongated separately to different percentages. Thus many specimens were obtained composed of crystals having various sizes.

For the special purpose of letting the crystals grow larger, the elongation of about 1.5% was given to the rods, and eighteen specimens having crystals of linear size from 9 cm. to 15 cm. were obtained. The surfaces of the specimens were slightly etched with dilute solution of hydrochloric acid so as to make the crystals clearly visible. For each rod thus etched, its diameter was measured at several parts with a micrometer screw guage, and the average value was taken. The stress exerted on the rod was expressed by the load applied to it per unit initial area.

In order to determine the orientation of the crystal in each rod composed of a large single crystal, one side of the rod was illuminated

perpendicularly by an X-ray beam. From the distribution of the Laue-spots thus produced on a photographic plate, the orientation of the crystal was determined by means of the crystallographic globe devised by Prof. U. Yoshida.[1] The orientations of the crystals of 18 rods examined are shown by a stereographic projection in Fig. 1. In this figure the longitudinal direction of the rod is represented by a dot referring to the three crystallographic axes [100]. The writer measured small elongations of the above-mentioned specimens by means of the extensometer previously designed by him,[2] and plotted the curve showing the relation between the stress per unit area and the elongation per unit length. From this curve he determined the elastic limit of the specimen by using the contact point finder previously reported by him.[3] Linear grain number and linear crystal size were measured by examining the etched surface of the specimen by a travelling micrometer.

Fig. 1



Experimental Result

The guage length employed in the present experiment was 10 cm., so that in the case of the specimens having the linear crystal size a little shorter than 10 cm., another crystal having different orientation was contained within the guage length. But the effect of this fact was negligible. The result of the measurements is shown in Table I. As is seen from this table, the limit of elasticity expressed by the elongation per unit length, takes various values from 2.2×10^{-5} to

1. U. Yoshida, Jap. J. Phys., **4**, 133, (1927).
2. These Memoirs, A, **20**, 19, (1937).
3. These Memoirs, A, **20**, 27, (1937).

3.15×10^{-5}. It is very difficult to determine acculately the elastic limit, and the limit of the experimental errors was estimated to be about $\pm 0.4 \times 10^{-5}$ in the present case. Hence it seems legitimate to state that the limit of elasticity is almost the same for all the specimens tabulated in Table I, irrespective of the crystal orientations. To examine this point more clearly, the values multiplied by 10^5 of the elastic limits were respectively written under the dots in Fig. 1, which show the orientations of the longitudinal directions of the rods. In this figure, no systematic change of the values of the elastic limit with the difference of the crystal axes can be detected. Consequently it may be stated that the limit of elasticity is almost independent of the orientation of the crystal. Thus by taking the average for different specimens of various crystallographic orientations, the value 2.52×10^{-5} was obtained for the limit of elasticity of a single crystal of aluminium.

Table I

Specimen	Limit of elasticity		Young's Modulus
No.	Stress per unit area	Elongation per unit length	in C. G. S. unit
1	15 $\frac{kg}{cm^2}$	2.20×10^{-5}	6.68×10^{11}
2	15	2.20	6.68
3	17	2.45	6.80
4	18	2.63	6.71
5	17.5	2.55	6.73
6	15	2.20	6.68
7	22	3.15	6.84
8	15	2.20	6.68
9	17	2.46	6.77
10	21	3.05	6.75
11	18	2.62	6.73
12	15	2.20	6.68
13	22	3.15	6.84
14	15	2.20	6.68
15	16	2.32	6.76
16	16	2.32	6.76
17	21	3.00	6.83
18	17	2.45	6.76
Average	17.4	2.52	6.74

For each different group of the specimens composed of crystals smaller than the above, the average values of the elastic limit and the grain number were taken respectively by examining five or six specimens belonging to the same group. Such an example is given in Table II.

For ten different groups of the specimens, the elastic limit, the Young's modulus, the grain number and the crystal size are given in Table III, where the grain number and the crystal size are mutually

Table II

Specimen	Limit of elasticity		Young's Modulus	Grain number per unit length
No.	Stress per unit area	Elongation per unit length	in C. G. S. unit	per one cm.
1	28 $\frac{kg}{cm^2}$	4.1×10^{-5}	6.69×10^{11}	14
2	27	3.9	6.78	13.5
3	30	4.3	6.84	13
4	27	3.9	6.78	15
5	32	4.6	6.81	14.5
6	27.5	4.0	6.74	14
Average	28.6	4.13	6.77	14

Table III

Specimen	Limit of elasticity		Young's modulus	Grain Number per unit length	Linear grain size
Group Number	Stress per unit area	Elongation per unit length	in C. G. S. unit	per one cm.	
1	17.4 $\frac{kg}{cm^2}$	2.52×10^{-5}	6.74×10^{11}	0.100	10 cm.
2	19.2	2.77	6.73	0.22	4.5
3	22.8	3.31	6.77	3.54	0.282
4	28.6	4.13	6.77	14	0.072
5	39.6	5.76	6.74	54	0.019
6	50.8	7.38	6.75	197	0.005
7	54.2	7.83	6.78	301	0.003
8	64.6	9.44	6.70	506	0.002
9	81	11.9	6.68	773	0.0013
10	98	14.4	6.68	1049	0.00095

reciprocal. From the table, it is seen clearly that the Young's modulus has the same value within the limit of experimental errors for all the specimens as has been previously reported by the writer.[1] In this table, the numbers in the last two horizontal rows are taken from the previous report,[2] for the sake of comparison.

The curve showing the relation between the limit of elasticity and the linear grain number is given in Fig. 2, where the small dots denote the values observed in the present experiment and the small circles those in the previous one. It is clearly seen from the curve,

1. These Memoirs, A, **17**, 389, (1934).
2. These Memoirs, A, **20**, 27, (1937).

Fig. 2

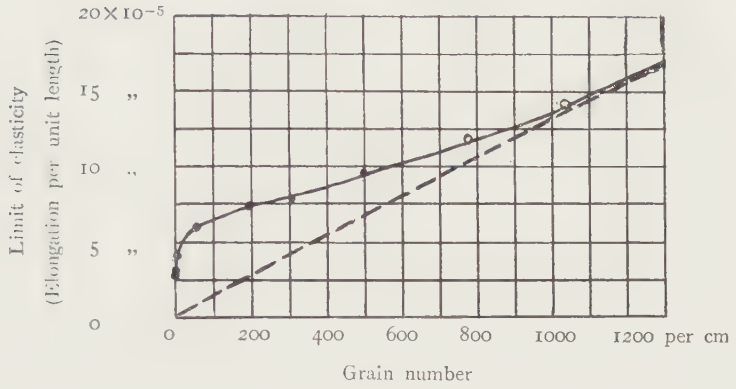
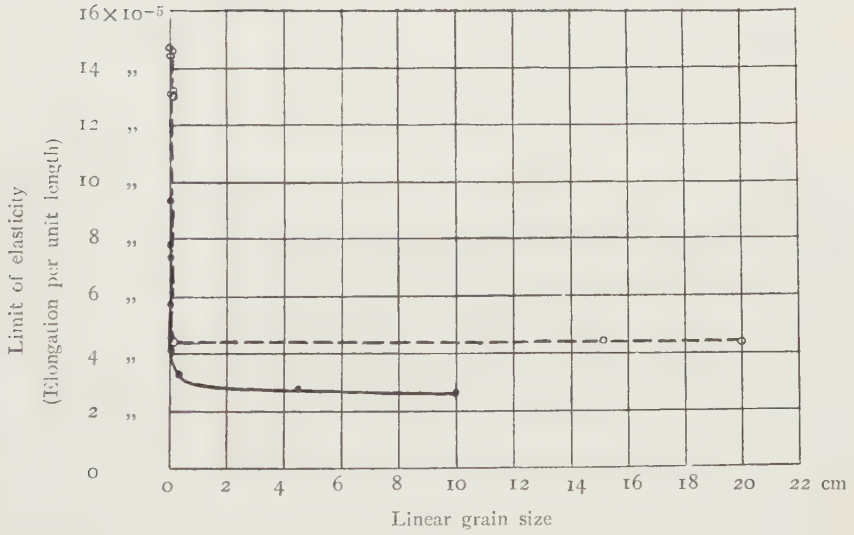


Fig. 3



that the connection of the present result and the previous one is perfect. The broken line denotes the extension of the empirical formula obtained previously for comparatively small crystals.[1] The disagreement between these two curves becomes larger with the decrease of grain number. Accordingly the empirical formula can not be applied to the case of the large grain size.

Fig. 3 shows the relation between the limit of elasticity and the linear grain size. From this figure it is clearly found that the limit

1. These Memoirs, A, **20**, 27, (1937).

of elasticity decreases rapidly with the increase of the grain size, and after exceeding the grain size of about 0.3 cm. it decreases very slowly.

In order to compare the present result with the previous one,[1] the elongation per unit length and the linear grain size are calculated respectively from the values of the stress per unit area and the areal grain size given in the previous report, and they are tabulated in Table IV. The broken line in Fig. 3 represents the result given in Table IV, and shows a similar tendency as the above-mentioned one; but it gives somewhat greater values for the elastic limit than the other does. This discrepancy between the two results is due to the difference of procedure for measuring the elongation. For the broken line, the following procedure was followed. By the application of a certain load to the rod, its elongation was measured, and on its removal the permanent set was measured; and again by applying a larger load, its elongation and the set caused by the release of the load were measured. Such an operation was repeated several times until a well-defined and increasing permanent set was reached. This procedure seems to distort the crystals somewhat, and gives a larger value for the elastic limit. Thus such a procedure is not suitable for measuring the elongation of the rod composed of larger crystal grains.

Table IV

Specimen No.	Limit of elasticity: Elongation per unit length	Linear grain size
1	4.37×10^{-5}	20 cm.
2	4.44	15
3	4.42	0.1
4	13.22	0.05
5	13.09	0.04
6	13.28	0.03
7	14.65	0.03
8	14.81	0.02
9	14.48	0.02

In conclusion, the writer wishes to express his sincere thanks to Prof. U. Yoshida for his kind guidance in the research.

1. These Memoirs, A, **17**, 389, (1934).

The Fibrous Arrangement of the Micro-Crystals of Silver Chloride

By

Shin'ichi Shimadzu

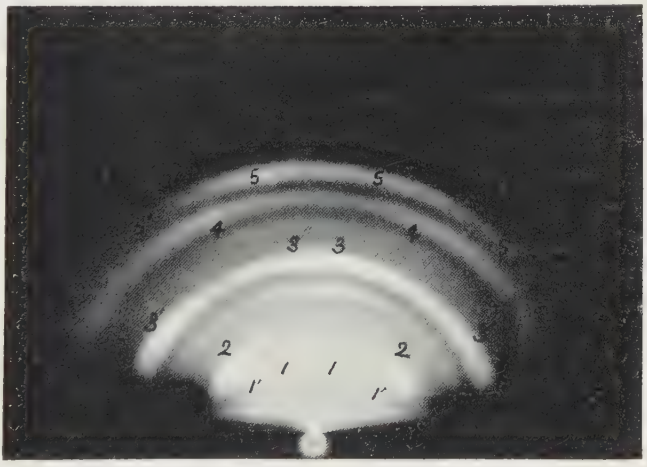
(Received June 25, 1937)

Abstract

A diffraction pattern showing a fibrous arrangement of the micro-crystals of silver chloride was obtained by sending the characteristic X-rays of copper obliquely to the surface of a silver plate which had been dipped for a long time in chlorine water. The writer found that the fiber axis was parallel to the [331] axis of the crystal of silver chloride and was perpendicular to the surface of the silver plate.

The fibrous X-ray photograph shown in Fig. 1 was obtained by sending the K radiation of copper obliquely to the surface of a silver plate which had been dipped in chlorine water for more than fifty hours. So long as the inclination of the X-ray beam to the surface of the silver plate is constant, the same X-ray patterns are always obtained, even if the plate is placed at different orientations. This fact indicates that the fiber axis is perpendicular to the surface of the silver plate. Also, the same pattern was obtained with both annealed and rolled silver plate, and hence it appears that the manner of the arrangement of the micro-crystals of silver chloride is independent of the grain size and the arrangement of the micro-crystals of silver in silver plate.

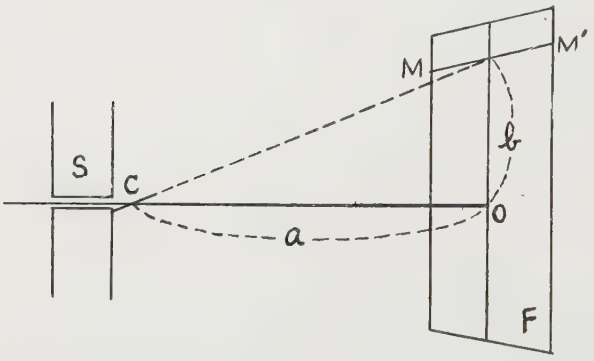
Fig. 1



The photograph reproduced in Fig. 1 was obtained as follows. In Fig. 2 the X-ray beam through the slit S illuminates the silver plate C which is placed just behind S obliquely for the X-ray beam. In order to obtain on the same photographic plate the image of the central spot where the X-ray beam strikes the photographic plate directly, the silver plate was removed and a short second exposure was made on the same photographic plate which had already received the long exposure while the silver plate was in position.

The angle δ of the inclination of the X-ray beam for the surface of the silver plate was found of the following way: As the crystal structure of silver chloride is known, the indices and consequently the lattice constants of the atomic planes corresponding to the circular arcs on the photograph were obtained from the radii of the circular arcs and the rough value of the distance a between the silver plate C and the photographic plate F which was set normal to the incident X-rays. In order to get the accurate value of δ, more accurate value of a is required; and this was calculated reversely from the radii of the circular arcs and the lattice constants of the corresponding atomic planes obtained as above. Next, let the line of intersection of the plane including the surface of the silver plate and the photographic plate be MM′, which appears as a shadow line on the X-ray photograph; then when the distance b from the central spot O to MM′ is measured, we can get the value of δ from the relation

Fig. 2



$$\tan\delta = b/a.$$

The value of δ thus determined was 15° in the case of Fig. 1.

Now, as the value of δ is found, we can determine roughly the direction of the fiber axis by using the crystallographic globe.[1] The writer found roughly that the fiber axis was perpendicular to the sur-

1. U. Yoshida: Japanese J. Phys., **4**, 133 (1927).
S. Takeyama: These Memoirs, **12**, 257 (1929).

face of the silver plate and was parallel to the axis [110] or [331] of the crystal of silver chloride.

In Fig. 3 AC is the direction of the incident X-rays, CN the normal to an atomic plane, the plane POD the photographic plate which is normal to the incident beam, P the position of the image of the reflected rays on the photographic plate, CB the direction of the fiber axis and OD is the line of intersection of the plane ABC and the photographic plate. If the angles α, β, γ and ε are taken as shown in Fig. 3, then we get the relation

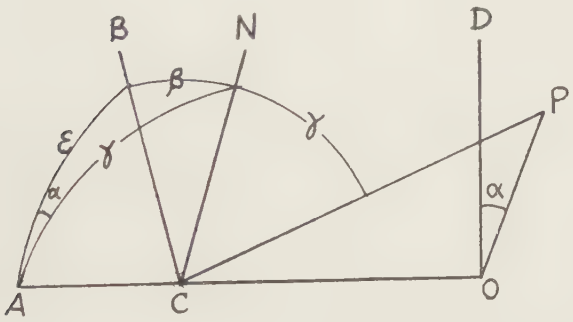
$$\cos\beta = \cos\gamma\cos\varepsilon + \sin\gamma\sin\varepsilon\cos\alpha. \qquad (1)$$

As $\varepsilon = \frac{\pi}{2} - \delta$, we can get the value of $\cos\beta$ for each atomic plane from the above formula.

Next, take the three edges of a unit cell of the cubic crystal as the rectangular coordinate axes; and let the direction cosines of the fiber axis be l, m, n and those of the normal to an atomic plane be l', m', n' as shown in Fig. 4, then we get the following relation

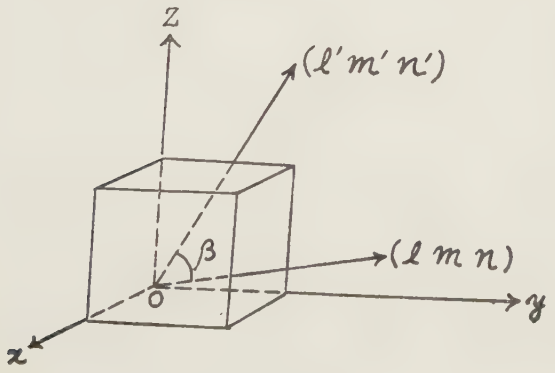
$$\cos\beta = ll' + mm' + nn'. \qquad (2)$$

Fig. 3



If the direction of the normals to three different atomic planes is given, then we can get the values of l, m and n. In the present case the writer found the values of $\cos\beta$ for the most intense spots in the circular arcs 1, 2 and 3 in Fig. 1. As these circular arcs belong respectively to the atomic planes (111), (200) and (220) of the cubic crystal of silver chloride, the values of l', m' and n'

Fig. 4



for these atomic planes are readily calculated. By inserting the values of l', m', n' and $\cos\beta$ thus obtained in the equation (2), we obtain three linear equations containing l, m and n; and by solving these equations the writer obtained the following values for l, m and n

$$l=0.702, \qquad m=0.683, \qquad n=0.203.$$

On the other hand, the direction cosines of the [110] axis are

$$l=m=0.708, \qquad n=0,$$

and those of the [331] axis are

$$l=m=0.689, \qquad n=0.229.$$

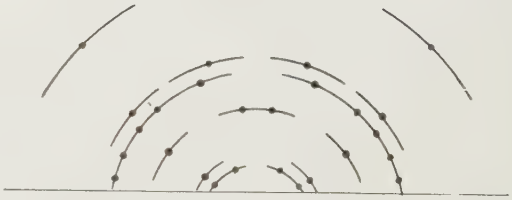
Then it seems better to take the [331] axis as the fiber axis than the [110] in the present case.

The values of the angle γ for an atomic plane is calculated easily for a given wave length of the X-rays. As the values of the angles ϵ and β are also obtained for a given fiver axis, the angle α is calculated readily with equation (1). In such a manner we can draw a diffraction pattern for a given fiber axis. Figs. 5 and 6 are the fibrous patterns thus drawn respectively by taking the [110] and the [331] axes as the fiber axes and by taking $\delta=15^\circ$ as was actually observed. In these figures dots are the calculated positions of the spots when the microcrystals arrange themselves in the fibrous manner perfectly and the circular arcs indicate the diffraction patterns obtained actually on the photographic plate. In Fig. 5 where [110] was taken as the fiber axis there are no spots corresponding to the arcs 3 and 5 in Fig. 1. Whereas in Fig. 6 where [331] was taken as the fiber axis the dots are present favourably in positions corresponding accurately to all the prominent arcs. Here it must be mentioned that the arc 4 is to be considered as composed of

Fig. 5

[110]

Fig. 6



[331]

many arcs and thus it appeared as a long continuous arc on the photograph. From these facts it seems almost certain that the fiber axis of the micro-crystals of silver chloride is parallel to the [331] axis and perpendicular to the surface of the silver plate.

The writer obtained an identical fiber photograph with a silver plate which was exposed to the chlorine gas. This seems to support the view that the fibrous arrangement of the micro-crystals of silver chloride as is stated above is mainly due to the nature of the micro-crystals themselves and not the mode of depositting the micro-crystals on the silver plate.

In conclusion, the writer wishes to express his sincere gratitude to Prof. U. Yoshida for his kind guidance during the course of this experiment.

On the Summation of an Expansion of Polynomials of Hermite

By

Tunezô Satô

(Received June 25, 1937)

Mr. N. Wiener has derived the following formula

$$\sum_{n=0}^{\infty} t^n \psi_n(x)\psi_n(y) = \frac{1}{\sqrt{\pi(1-t^2)}} \exp\left[\frac{4xyt-(x^2+y^2)(1+t^2)}{2(1-t^2)}\right],$$

where $\psi_n(x)$ represents the system of functions of Hermite. In regard to this formula, Mr. G. H. Hardy has made a note in his paper,[1] in which he said that he has never seen such formula. Recently I have read Mr. Wiener's book,[2] and found out that the method of proof of the formula as he gives it is rather complicated.

In this paper I treat this formula, simplifying it to some extent, and suggesting more general formula which seems to me better. But original idea is of course based on the suggestion in Mr. Wiener's method.

The function $K(x_1, x_2, \ldots\ldots, x_\nu ; t)$ is defined over any finite complex domain of $x_1, x_2, \ldots\ldots, x_\nu$ and the complex plane of t. Even more it satisfies the four following hypotheses:

(I) each of K, $\dfrac{\partial K}{\partial x_i}$ and $\dfrac{\partial^2 K}{\partial x_i \partial x_j}$ $(i, j = 1, 2, 3, \ldots\ldots, \nu)$ has only two points $t = \pm 1$ as isolated singular points in the complex plane of t and is elsewhere regular,

(II) when expanded as a series in powers of t, each of $K(x_1, \ldots\ldots, x_\nu ; t)$, $K(x, x, \ldots\ldots, x ; t)$, $\dfrac{\partial K}{\partial t}$, $\dfrac{\partial^2 K}{\partial x_i^2}$ and $\dfrac{\partial K}{\partial x_i}$ is respectively dominated by the expansion of some corresponding function over $|x_i| < \mathfrak{A}_i$,[3] which is analytic in t for $|t| < 1$,

(III) K satisfies the partial differential equation

---

1. "Summation of a series of polynomials of Laguerre," Jour. of the London Math. Soc., vol. VII. (1932).

2. "The Fourier integral and certain of its applications," Camb. pp. 51–62.

3. It is noticed that $\mathfrak{A}_i$ can be taken for any finite positive number.

(L) $\dfrac{\partial^2 K}{\partial x_i^2}-x_i^2 K=-2t\dfrac{\partial K}{\partial t}-K$, $(i=1, 2, 3, \ldots\ldots, \nu)$

(IV) if we put $\dfrac{1}{n!}\left[\dfrac{\partial^n K}{\partial t^n}\right]_{t=0}=K_n$, $(n=1, 2, 3, \ldots\ldots)$ then K_n and $\dfrac{\partial K_n}{\partial x_i}$ vanish together as $|x_i|\to\infty$.

To begin with, by Taylor's expansion,

$$(1)\quad K(x_1, \ldots\ldots, x_\nu; t)=\sum_{n=0}^{\infty}\frac{1}{n!}\left[\frac{\partial^n K}{\partial t^n}\right]t^n$$
$$=\sum_{n=0}^{\infty}K_n(x_1, \ldots\ldots, x_\nu)t^n, \text{ for } |t|<1.$$

From the hypothesis (II), if $|t|<1$, the series of the above second member converges uniformly as to all ν-variables $x_1, x_2, \ldots\ldots, x_\nu$. Since the expression (1) satisfies the given partial differential equation (L), it results at once that

$$\frac{\partial^2 K_n}{\partial x_i^2}-x_i^2 K_n=-(2n+1)K_n.$$

Now if we put

$$(2)\quad K_n(x_1, x_2, \ldots\ldots x_\nu)=A_n(x_1, x_2, \ldots\ldots, x_\nu)e^{-\frac{x_1^2+x_2^2+\cdots+x_\nu^2}{2}},$$

we have

$$(3)\quad \frac{\partial^2 A_n}{\partial x_i^2}-2x_i\frac{\partial A_n}{\partial x_i}+2nA_n=0.$$

Here we consider two differential equations as follows

$$(L_1)\quad \frac{d^2 z}{dx^2}-x^2 z+(2n+1)z=0,$$

$$(L_2)\quad \frac{d^2 z}{dx^2}-2x\frac{dz}{dx}+2nz=0.$$

The differential equation (L_1) has one and only one solution which satisfies such boundary conditions that z and $\dfrac{dz}{dx}$ vanish together as $|x|\to\infty$; for, let z_1 and z_2 be two such solutions of (L_2), then we have

$$z_1''-x^2 z_1=-(2n+1)z_1 \text{ and } z_2''-x^2 z_2=-(2n+1)z_2.$$

By multiplying the first equation by z_2, the second by z_1, and subtracting the one from the other, it may be obtained that $(z_1'z_2-z_2'z_1)'=0$, accordingly $z_1'z_2-z_2'z_1=const.$; here let $|x|\to\infty$, then we have $const.=0$. This contradicts the independency of z_1, z_2.

Now as it is well known that the differential equation (L_1) has the solution $H_n(x)e^{-\frac{x^2}{2}}$ as the unique solution which satisfies the above stated boundary conditions, where $H_n(x)$ is a solution of the

differential equation (L_2), we can conclude by the hypothesis (IV) that $K_n(x_1, x_2, \ldots\ldots, x_\nu) = H_n(x_i)e^{-\frac{x_i^2}{2}}\varphi(x_1, \ldots\ldots, x_{i-1}, x_{i+1}, \ldots\ldots x_\nu)$ necessarily, where the factor φ is independent of the variable x_i.

Thus we have

$$(4)\quad A_n(x_1, x_2, \ldots\ldots x_\nu) = d_n H_n(x_1)H_n(x_2)\ldots\ldots H_n(x_\nu),$$

where $H_n(x)$ means Hermite polynomial and d_n a pure constant to be determined in the sequel.

As previously shown, it is necessary that every function $A_n(x_1, x_2, \ldots\ldots, x_\nu)$ must be a polynomial of ν variables $x_1, x_2, \ldots\ldots, x_\nu$ and symmetric with respect to these variables.

Hence from (1), (2) and (4) we have

$$(5)\quad K(x_1, \ldots\ldots x_\nu\,;\, t) = \sum_{n=0}^{\infty} d_n \phi_n(x_1)\phi_n(x_2)\ldots\ldots\phi_n(x_\nu)t^n,$$

where $\phi_n(x_i) = H_n(x_i)e^{-\frac{x_i^2}{2}}$. Here the system of functions $\phi_n(x)$ forms the orthogonal system of Hermite functions.

Now we wish to determine the values of coefficients of series (5), d_n. For the present purpose, let us consider the following series

$$(6)\quad \int_{-\infty}^{\infty} K(x, x, \ldots\ldots, x\,;\, t)dx = \sum_{n=0}^{\infty} c_n t^n,$$

for $|t| < 1$. By means of (5) it results that

$$K(x, x, \ldots\ldots x\,;\, t) = \sum_{n=0}^{\infty} d_n[\phi_n(x)]^\nu t^n.$$

Since the hypothesis (II) shows the uniform convergence of series in the right hand of the above expression, if we combine this with the expansion of the second member of (6), then we obtain

$$(7)\quad c_n = d_n \int_{-\infty}^{\infty} [\phi_n(x)]^\nu dx.$$

Now when we take as a value of $\left\{\int_{-\infty}^{\infty} [\phi_n(x)]^\nu dx\right\}^{\frac{1}{\nu}}$ a real one of ν roots of it, we have from (7) and (5)

$$(8)\quad K(x_1, \ldots\ldots, x_\nu\,;\, t) = \sum_{n=0}^{\infty} c_n \psi_n(x_1)\psi_n(x_2)\ldots\ldots\psi_n(x_\nu)t^n,$$

where

$$(8')\quad \psi_n(x_i) = \phi_n(x_i) \Big/ \left\{\int_{-\infty}^{\infty} [\phi_n(x_i)]^\nu dx_i\right\}^{\frac{1}{\nu}}.$$

We now return to functions by which the previous hypotheses (I), (II), (III) and (IV) are all satisfied. Because of simplification of our treatment, let $\nu = 3$. Let us consider such a particular function as

$$(9)\quad K(x, y, z\,;\, t) = A.\exp\{-B(x^2+y^2+z^2) + 2Cxy + 2Dyz + 2Ezx\}.$$

It is easy to verify that this function may satisfy hypotheses (I), (II)

and (IV). Thus we seek conditions that the function (9) may be a solution of the partial differential equation (L): in other words, relations to hold among the coefficients A, B, C, D and E, those which are functions of only t.

In the first place, put (9) into (L), then

$$-2t\{\alpha - B'(x^2+y^2+z^2)+2C'xy+2D'yz+2E'zx\}-1 \\ =-2B+4(Bx-Cy-Ez)^2-x^2,$$

where $\alpha=A'/A$ and dashes mean the derivatives with respect to t. Since this equation ought to hold identically with respect to x, y, z, it follows that

(i) $2tB'-4B^2+1=0$,
(ii) $tC'-2BC=0$,
(iii) $tE'-2BE=0$,
(iv) $tB'-2C^2=0$,
(v) $tD'+2CE=0$,
(vi) $tB'-2E^2=0$,
(vii) $2t\alpha+1-2B^2=0$.

Now if we replace (vii) by (i), we obtain

$$t\alpha'-\alpha-2t\alpha^2=0,$$

hence $(t/\alpha)'=-2t$. By integrating $\alpha=t/(\rho-t^2)$. While $\alpha=A'/A$. Again by integrating we deduce

$$A=\frac{a_0}{\sqrt{\rho-t^2}},$$

where ρ and a_0 are integral constants, but they are determined so as always $A(t)>0$ for all real t.

Thus from the remaining relations, it follows that

$$B=\frac{1}{2}\frac{\rho+t^2}{\rho-t^2}, \quad C^2=E^2=\frac{t^2\rho}{(\rho-t^2)^2}, \quad D^2=\frac{\rho^2}{(\rho-t^2)^2}.$$

However by means of the hypothesis (I), it needs that $\rho=1$. Therefore we have the following relations:

$$A=\frac{a_0}{\sqrt{1-t^2}}, \quad B=\frac{1}{2}\frac{1+t^2}{1-t^2}, \quad C^2=E^2=\frac{t^2}{(1-t^2)^2},$$

$$D^2=\frac{1}{(1-t^2)^2}.$$

Here we can give four pairs of values for C and E. Hence if we replace (9) by the above obtained results, we have in general four different functions as for K to be required. But to avoid repeating the same arguments we shall discuss only one of these functions; namely

$$(10)\quad K(x, y, z; t)=\frac{a_0}{\sqrt{1-t^2}}\exp\left\{\frac{-(1+t^2)(x^2+y^2+z^2)+4t(xy+xz)-4(1-t^2)yz}{2(1-t^2)}\right\}.$$

By evaluating the integral (6),

$$\int_{-\infty}^{\infty}K(x, x, x; t)dx=\frac{a_0}{\sqrt{1-t^2}}\int_{-\infty}^{\infty}e^{-\frac{7-4t-t^2}{2(1-t^2)}x^2}dx;$$

on the other hand, we see that the parabola, whose equation is $y=x^2+4x-7$, lies evidently under the X-axis in the interval $-1\leqq x\leqq 1$, hence for any real value of t such as $|t|<1$,

$$(7-4t-t^2)/2(1-t^2)>0.$$

Thus by the familiar integral formula,

$$\int_{-\infty}^{\infty}e^{-\frac{7-4t-t^2}{2(1-t^2)}x^2}dx=\sqrt{2\pi}\sqrt{\frac{1-t^2}{7-4t-t^2}},$$

therefore

$$\int_{-\infty}^{\infty}K(x, x, x; t)dx=a_0\sqrt{2\pi}(7-4t-t^2)^{-\frac{1}{2}}$$
$$=a_0\sqrt{2\pi}(c_0+c_1t+c_2t^2+\cdots\cdots)$$

$c_0=7^{-\frac{1}{2}}$, $c_1=2.7^{-\frac{3}{2}}$, $c_2=5.7^{-\frac{5}{2}}$,.....

Consequently from (8) we obtain the following formula

$$(11)\quad \frac{a_0}{\sqrt{1-t^2}}\exp\left\{\frac{-(1+t^2)(x^2+y^2+z^2)+4t(xy+xz)-4(1-t^2)yz}{2(1-t^2)}\right\}$$
$$=\sum_{n=0}^{\infty}c_n\psi_n(x)\psi_n(y)\psi_n(z)t^n,\ \text{for}\ |t|<1,$$

where $c_0=7^{-\frac{1}{2}}a_0\sqrt{2\pi}$, $c_1=a_0\sqrt{2\pi}.2.7^{-\frac{3}{2}}$, $c_2=a_0\sqrt{2\pi}.5.7^{-\frac{5}{2}}$,.....

and $\psi_n(x)=\phi_n(x)/\left\{\int_{-\infty}^{\infty}[\phi_n(x)]^3dx\right\}^{\frac{1}{3}}$, $\phi_n(x)=H_n(x)e^{-\frac{x^2}{2}}$.

In conclusion the author wishes to express his hearty thanks to Professor Toshizô Matsumoto for his kind advice during the study.

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CONTENTS

Note on the Rate of Evaporation of small Water Drops, such as Rain-Drops
By Tadao Namekawa and Tatutoshi Takahashi 139
A Method of Obtaining Fibrous Arrangements of the Micro-Crystals of Some Substances
By Noritomo Matsumoto 147
On the Pseudo-set
By Tameharu Shirai 153
Change of Lattice Constants of Fibroin by Perfect Drying
By Yoshiaki Matsunaga 157
Elastic Limit of an Aluminium Rod and the Size of the Crystal Grains
By Miyabi Sugihara 173
The Fibrous Arrangement of the Micro-Crystals of Silver Chloride
By Shin'ichi Shimadzu 179
On the Summation of an Expansion of Polynomials of Hermite
By Tunezô Satô 185